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Influence of $EDTA^{2-}$ on the hydrothermal synthesis of CdTe nanocrystallites

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ABSTRACT

Transformation from Te nanorods to CdTe nanoparticles was achieved with the assistance of EDTA as a ligand under hydrothermal conditions. Experimental results showed that at the beginning of reaction Te nucleated and grew into nanorods. With the proceeding of reaction, CdTe nucleus began to emerge on the surface, especially on the tips of Te nanorods. Finally, nearly monodispersed hexagonal CdTe nanoparticles with diameters of about 200 nm were obtained. The effects of EDTA on the morphology and formation of CdTe nanoparticles were discussed in consideration of the strong ligand-effect of EDTA, which greatly decreased the concentration of Cd^{2+}. Furthermore, the possible formation process of CdTe nanoparticles from Te nanorods was further proposed. The crystal structure and morphology of the products were investigated by X-ray diffraction (XRD) and scanning electron microscopy (SEM).

1. Introduction

Recently, considerable attentions have been paid to II–VI semiconductor materials because of their technical importance as electrical and optoelectronic components [1–3], light-emitting devices [4–6], nonlinear optical materials [7,8] and biological labels [9–11]. As an important II–VI semiconductor material, CdTe nanocrystals have been investigated as possible candidates for integration into light-emitting devices and for luminescent doping of photonic colloidal crystals. After a typical organometallic approach was introduced in the early 1990s [12], this synthetic scheme of CdTe nanocrsytals was considered to be an inspiring example and model system in this field. Although the organometallic synthesis has been ameliorated to eliminate its disadvantages such as poor reproducibility and the use of extremely toxic, expensive and explosive precursors, the selenium and tellurium precursors being used are closely related to organophosphorus compounds that are not very "green" at all [13]. In comparison, an aqueous synthesis of CdTe nanocrystals is simpler, greener and highly reproducible [14]. There are numerous reports regarding the synthesis of II–VI nanomaterials in aqueous phase by using inorganic cadmium salts as the cadmium precursor [15–17]. And we also researched on the preparation of CdTe nanocrystals under hydrothermal conditions [18]. CdTe nanocrystals prepared in aqueous solution are usually stable and have acceptable photoluminescence quantum yield at room temperature. However, their formation mechanism in aqueous solution especially in hydrothermal condition has rarely been reported in the open literature. In this study, we investigated the transformation process of CdTe crystallite from Te nanorods in the presence of EDTA, a strong ligand with Cd^{2+}.

2. Material and methods

All reagents used in this work, including cadmium nitrate ($Cd(NO_3)_2 \cdot 4H_2O$), sodium tellurite (Na_2TeO_3), ethylenediamine-terraacetic acid disodium salt (Na_2EDTA), ammonia solution ($NH_3 \cdot H_2O$) and hydrazine hydrate ($N_2H_4 \cdot H_2O$), were AR grade reagents obtained from China National Medicines Corporation Ltd. and were used directly without any treatment. All solutions were prepared with Mili-Q water (18.2 MΩ) as a solvent.

In a typical synthesis, 0.77 g $Cd(NO_3)_2 \cdot 4H_2O$ was dissolved in 10 ml saturated Na_2EDTA solution and the solution turned out to be a little turbid. After stirring for 5 min, 1 ml $NH_3 \cdot H_2O$ was added and the white precipitation disappeared. 2.5 ml Na_2TeO_3 (0.5 M) solution and 2.5 ml $N_2H_4 \cdot H_2O$ were added into the solution in sequence under continuous stirring until the solution became colorless and transparent. The obtained solution was then transferred to a 25 ml Teflon-lined stainless steel autoclave. The autoclave was filled with deionized water up to 90% of the total volume, sealed, and heated in an oven at 150 °C for an appropriate duration. After reaction, the autoclave was allowed to cool to room temperature naturally. Black product was obtained and collected by filtration, washed repeatedly with distilled water and absolute ethanol, and then dried in vacuum drier at 60 °C for 4 h.

X-ray diffraction (XRD) analysis was carried out on a Bruker D8 Advance X-ray diffractometer. The topographies of Te nanorods

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and CdTe nanoparticles were examined through a HITACHI S-4800 field emission scanning electron microscope (SEM). Element mappings of CdTe along with Te were performed under HORIBA EMAX Energy EX-350 energy dispersive spectrometer attached to S-4800 SEM. The excitation and emission spectra were recorded on an Edinburgh PL S920 fluorescence spectrophotometer at room temperature.

3. Results and discussion

3.1. Crystal structure analysis

The XRD patterns of products subjected to different reacting durations are shown in Fig. 1. All the diffraction peaks of pattern *a* can be indexed to hexagonal Te, which is in good agreement with the standard values in the literature (JCPDS no. 86-2269). From the pattern, the diffractions of planes (111) (220) (311) are well observed (marked with ■). No other impurities are detected in the sample. In contrast, pattern *d* is indexed to phase-pure and zinc-blended CdTe with lattice constant of $a=6.482$ Å in accord with JCPDS card no. 15-0770. The main diffraction planes such as (100) (101) (102) (110) are marked with ▲. However, the patterns of *b* and *c* have all the characteristic diffraction peaks of Te and CdTe, which confirm the coexistence of Te and CdTe.

The series of four patterns indicate that the initial stage was dominated by the nucleation and growth of Te crystallites. CdTe crystallites appeared gradually with the advance of reaction and their amount increased accordingly as evident from the intensities of diffraction peaks. It is certain that the nucleation and growth of CdTe will consume some Te, which results in the decrease of Te content. When the reaction completed, only CdTe remained and Te was exhausted. Our previous experiments without the presence of EDTA showed that there was only CdTe even in very short reaction duration [18]. This suggested that EDTA played an important role in the process of reaction and it impetuses us to perform this study.

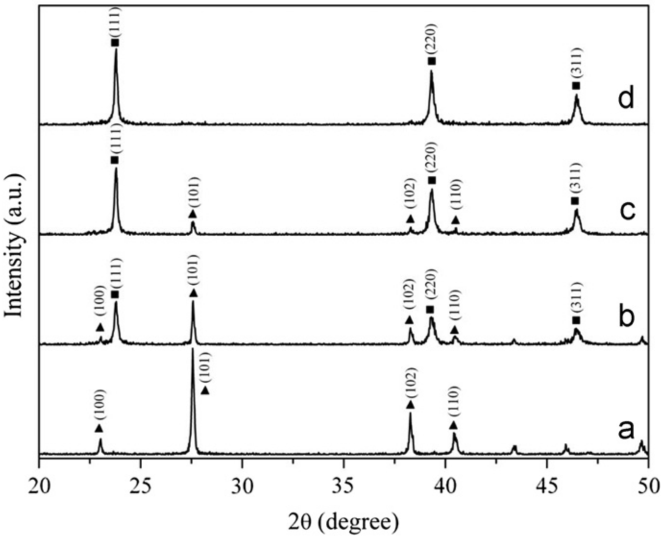

Fig. 1. XRD patterns of samples acquired at different reacting stages ((a)–(d) represent the different reaction durations 2 h, 6 h, 12 h and 36 h, respectively). The diffraction peaks of CdTe and Te are marked with ■ and ▲, respectively.

3.2. Morphology observation at different stages

Fig. 2 shows typical SEM images of these four samples for different reacting durations. Firstly, the products were only nanorods with diameters of about 100 nm with lengths up to 1–2 μm (an aspect ratio of approximately 10–20). Many researchers have reported their synthesis of one dimensional (1D) Te nanomaterials [19–21]. The reasons for the formation of 1D Te nanomaterials will be discussed in the following text. With the progress of reaction, there were nanoparticles formed with diameters of 200–500 nm and their amount increased gradually. In the meaning while the originally formed nanorods reduced in number and so both nanorods and nanoparticles coexisted in the system as shown in Fig. 2b and c. Finally, the nanorods disappeared completely and only nanoparticles left.

In order to obtain insightful information on the composition of both nanorods and nanoparticles, we performed element mapping with energy disperse spectrum (EDS). The element-mapping function attached on EDS analysis provides us a useful tool to distinguish one element from another. The position of every element exist in one sample was marked with bright points and brighter position represent more element content. A nanorod with nanoparticles on it was chosen as the object and the results were shown in Fig. 3. It can be seen that Te elements exist not only in the nanorod but also in the nanoparticles as revealed by the "Te map" picture, but the Cd mapping ("Cd map" picture) shows that Cd element only exist in the particles. Therefore, it can be concluded that the nanorods consist of Te while the nanoparticles are CdTe.

3.3. Growth mechanism analysis from Te to CdTe

The reaction to form CdTe nanocrystallites can be described as follows:

$$TeO_3^{2-}+N_2H_4\cdot H_2O\rightarrow Te(\downarrow)+N_2(\uparrow)+2H_2O+2OH^- \quad (1)$$

$$2Te+N_2H_4\cdot H_2O+4OH^-\rightarrow 2Te^{2-}+N_2(\uparrow)+5H_2O \quad (2)$$

$$Cd^{2+}+Te^{2-}\xrightarrow{EDTA}CdTe(\downarrow) \quad (3)$$

In these reactions, Na_2TeO_3 serves as an excellent water-soluble Te source and can be readily reduced to Te by hydrazine hydrate in hydrothermal conditions. The newly produced Te with high reactivity will nucleate and grow into nanorods (Eq. (1)).

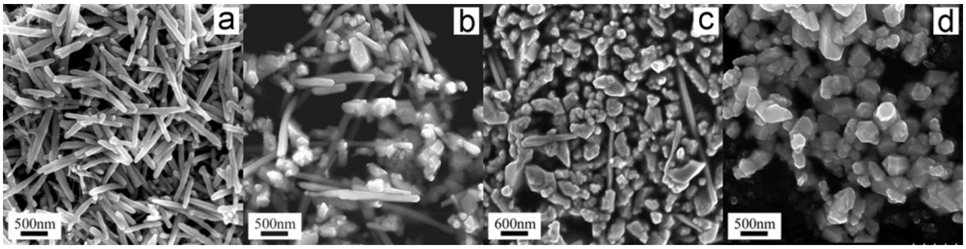

Fig. 2. SEM images of samples from Te nanorods to CdTe nanoparticles at different growth stages ((a) 2 h; (b) 6 h; (c) 12 h; and (d) 36 h).

With the proceeding of reaction, the formed Te nanorods will be reduced further by hydrazine (Eq. (2)) to Te^{2-}. Te^{2-} would react with Cd^{2+} to produce cadmium telluride nucleus on the surface of Te nanorods and finally grow into CdTe nanoparticles (Eq. (3)).

Experimental results indicated that reacting temperature had a significant effect on the rate of reaction, but was neglectable to the final product and chemical mechanism in the whole synthesis. Product formed at longer reacting time and lower temperature are prone to the same results as at elevated temperature while short reacting duration (not shown here). The effect of Cd/Te ratio is also insignificant. But the ratio of Cd/EDTA is a notable aspect because EDTA has a strong ligand effect with Cd^{2+} and the content of EDTA determined the final concentration of Cd^{2+} and the reaction products.

It is widely known that the coordinating reaction of EDTA with most heavy metal cations can take place with ratio of 1:1. Here, in our above experiment the molar ratio of Cd^{2+}:EDTA is 1:1.5. So EDTA is superfluous with respect to Cd^{2+} and there is only a minim of unsaturated Cd-EDTA (that is, freely Cd^{2+}). It is just the minimum Cd^{2+} that reacts with increasing Te^{2-} to form CdTe. Other ratios of Cd to EDTA (1:0.5, 1:1, 1:3) were also adopted to support the chemical mechanism. As the value of Cd/EDTA is 1:0.5, the reaction products were CdTe no matter how long the reaction duration was, just as the phenomenon of without EDTA [18]. With respect to 1:1 (without superfluous EDTA), CdTe nanoparticles had been formed on the Te nonorods within 2 h (Fig. 4a) and only CdTe left with 6 h reaction (Fig. 4b). However, when the content of EDTA was as high as three times of Cd^{2+}, the excessive EDTA prevented the formation of CdTe and Te to grow into rod-like structure with the progress of reaction (Fig. 4c and d). So, EDTA had a most important effect on the formation mechanism of CdTe and this further proved the rationality of our chemical mechanism.

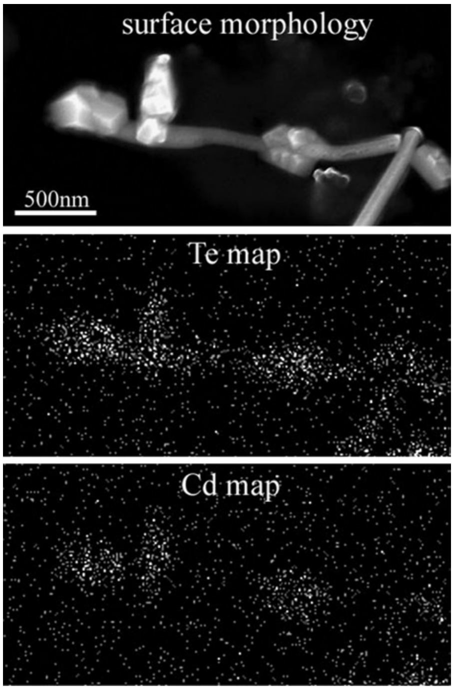

Fig. 3. Element maps of a single nanorod with nanoparticles on it.

From the above discussion, we know that the formation of CdTe nanoparticles is at the expense of Te nanorods. So, there was Te formed initially and CdTe next. A possible formation mechanism of CdTe nanoparticles is shown in Fig. 5. In hydrothermal conditions Na_2TeO_3, serving as a Te source, can be readily reduced to highly reactive free Te atoms by hydrazine hydrate. The newly formed Te with high reactivity can be further reduced to give birth to Te^{2-}. So both free Te atoms and Te^{2-} coexist in the solution and there exists a balance between them during the reaction. For the convenience of illustration, we prescribe the concentration of free Te atoms as [Te] and therefore Ksp(Te) as [Te] mol^{-1} L. Theoretically, Ksp(CdTe) is smaller than Ksp(Te) and therefore when EDTA is absent, CdTe nucleates and grows in the initial stage. However, the existence of EDTA affects greatly the concentration of Cd^{2+} because of their mutual strong ligand-effect. This makes the value of $[Cd^{2+}][Te^{2-}] \ll$ Ksp(CdTe) such that the formation of CdTe is thermodynamically prohibited. In contrast, when the concentration of free Te atoms reaches its nucleation threshold, Te nuclei will form and begin to grow. With the progress of reaction, Te grows into rods rather than sheets or particles. The most cited classic model for shape-control is the Wulff facets theorem [22], which suggests that the shape of a crystal is determined by the relative specific surface energy of each facet of the crystal, giving a minimum total surface energy [23]. Te has a highly anisotropic crystal structure consisting of helical chains of covalently bound atoms, thus having a strong tendency toward 1D growth [24].

Because of the coexistence of free Te atoms and Te^{2-} the increasing concentration of free Te atoms promotes the content of Te^{2-} with the development of reaction while the concentration of Cd^{2+} is nearly invariable. When the value of $[Cd^{2+}][Te^{2-}]$

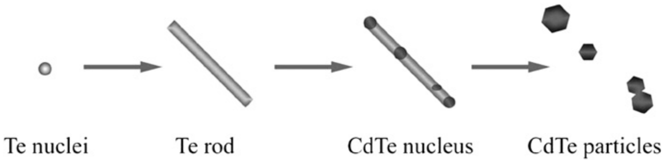

Fig. 5. Possible formation mechanism of CdTe nanoparticles from single crystal Te with existance of EDTA under hydrothermal conditions.

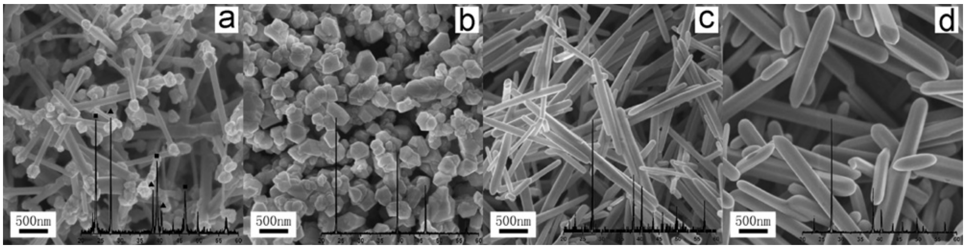

Fig. 4. SEM images of Te nanorods and CdTe nanoparticles with Cd/EDTA = 1:1 for 2 h (a) and 6 h (b), Cd/EDTA = 1:3 for 2 h (c) and 36 h (d), respectively, at 150 °C. The XRD patterns were also inserted into each figure to recognize the phases of CdTe and Te. The diffraction peaks of CdTe and Te in (a) were distinguished with squares (■) and triangle (▲), respectively.

exceeds Ksp(CdTe), the supersaturated CdTe begins to nucleate and grows. We suppose that the nucleation of CdTe may happen preferably at the tips of Te nanorod although we cannot rule out the possibility of nucleation in the middles of Te nanorods. The nucleation of CdTe may occurs in locations where there are more defects, which make nucleation more easily because of the existence of relatively more free energy. But the real mechanism requires further validation and we are working over it.

The formation of CdTe nucleus greatly decreases the free energy of the reacting system and it induces a whole avalanche. From then on, CdTe particles grow continuously in the expense of Te crystallites and the content of Te crystallites decreases along. Finally, Te nanorods are consumed out and only CdTe nanoparticles remain. Furthermore, the shape of CdTe nanoparticles may also be affected by EDTA. CdTe nanoparticles obtained without EDTA tends to be of irregular shape while the presence of EDTA tends to create nanoparticles with hexagonal symmetry (in Fig. 2d). The reason for this may be that the absorbance of EDTA on some specific facets of CdTe nanoparticles, which changes its growth rate on these facets and the nanoparticles finally evolve into the shape observed.

4. Conclusion

In conclusion, in the presence of EDTA, serving as a strong ligand with Cd^{2+}, we synthesized CdTe nanoparticles under hydrothermal conditions. And EDTA has a significant effect on the formation process of CdTe nanoparticles. In addition, the final morphology of CdTe nanoparticles may also be affected by EDTA. The existence of EDTA, which can decrease the concentration of Cd^{2+} greatly in solution, constrains the nucleation of CdTe and therefore high-reactive free Te atoms can nucleate and grow into nanorods. So this mechanism may provide us a thought of pure-phase Te crystallites growth by ruling out the effect of heavy metals with their corresponding strong ligands.

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