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Synthesis of CdTe Nanocrystals Using Te Nanorods as the Te Source and the Formation of Microtubes with Red Fluorescence

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Here, we report an alternative route to the preparation of highly luminescent CdTe nanocrystals (NCs) using Te nanorods instead of freshly prepared NaHTe as the Te source via a one-pot route under hydrothermal conditions. Furthermore, microtubes with red fluorescence were generated via simply aging the above CdTe NC suspension under ambient conditions.

Introduction

Semiconductor nanocrystals (NCs) have attracted wide attention because of their variety of size- and shape-dependent optical and electrical properties.[1−5] Over the past 20 years, many research groups have developed a rich variety of methods to synthesize highly fluorescent II−VI semiconductor NCs.[3,6−9] In general, the synthesis of II−VI semiconductor NCs can be classified as the following two rudimentary approaches: the organometallic precursor-based (often referred to as TOPO) route[3,6] as well as the aqueous-based route.[8,9] As an excellent example of organometallic precursor-based synthesis, the trioctylphosphine (TOP)/trioctylphosphine oxide (TOPO) synthetic route has become one of the most successful and mature approaches for fabricating highly fluorescent II−VI NCs, in which chalcogen−TOP made by dissolving chalcogen powder in TOP was used as the source of chalcogens.[3,7] Although the as-prepared NCs have both good monodispersity and photoluminescence, they are generally capped with hydrophobic ligands, which blocks the direct application in biosystems. As an alternative to the TOPO route, the aqueous-based preparation of thiol-capped NCs, which was pioneered by Weller et al.,[8] can provide products with excellent water solubility, stability, and biological compatibility.[8,10] In the case of the aqueous-based route, there are three factors used to determine the fluorescence of CdTe NCs: the tellurium precursor, the heating method, and the capped ligand (i.e., thiol). Generally, either H_2Te (a highly toxic and flammable gas) or NaHTe (an unstable compound because of its spontaneous oxidation in the presence of oxygen) was utilized as the tellurium precursor, but it resulted in an inert atmosphere.[8,11−13] More recently, alternative Te sources, such as Na_2TeO_3 and $(NH_4)_2Te$, were also used as tellurium precursors to obtain highly fluorescent CdTe NCs.[14,15] However, most of the above tellurium precursors not only usually require inert reaction systems but also have to be stored under an inert atmosphere. Otherwise, they would be spontaneously oxidized to the tellurium element by oxygen,[16,17] which has been employed by some groups to

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synthesize tellurium nanorods (NRs).[18] On the other hand, to synthesize high-quality CdTe NCs rapidly, both hydrothermal[9] and microwave irradiation methods[12,19,20] were developed on the basis of conventional refluxing methods. For example, He et al. have reported that high-quality CdTe (photoluminescence quantum yields (PL QYs) reached 82%, and the full width at half-maximum (fwhm) was as narrow as 27 nm) was successfully synthesized, assisted by microwave dielectric heating.[20] As for the kind of thiol, the previous report has revealed that the PL QYs of the CdTe NCs were dependent on the nature of the capped ligands.[15] Various kinds of thiols, such as 3-mercaptopropionic acid, thioglycolic acid, L-cysteine, mercaptosuccinic acid (MSA), and tripeptide glutathione, were used as stabilizers to synthesize high-quality CdTe NCs.[9−15,19,20] For instance, our group has demonstrated that the PL QYs of CdTe are about 10% when L-cysteine was used as the stabilizer and much higher at 35% when MSA was used as the stabilizer.[15] To our knowledge, there are few reports to prepare II−VI NCs using bulk tellurium as the precursor in an aqueous solution, which may result from the slow reaction rate between the bulk tellurium powder and reductants such as $NaBH_4$.[8,9] It is well-known that nanostructured materials inherently possess high chemical activity owing to their large surface-to-volume ratio.[21] Can we obtain high-quality II−VI NCs using nanostructured chalcogen as the precursor via the aqueous route? Herein, we demonstrated that high-quality CdTe NCs could be fabricated via the reaction between $CdCl_2$ and NaHTe, which was generated through an in situ reduction reaction of Te NRs with $NaBH_4$. Different from the previous aqueous route, in which NaOH was used to adjust the pH value to alkaline conditions,[9−14] here, both sodium citrate and $NaBH_4$ were used to adjust the pH value of the precursor solution. In the present route, MSA, a kind of thiol, was used as the stabilizer, which has been demonstrated to obtain a higher QY.[15] As for the heating method, a hydrothermal technique was exploited to synthesize high-quality CdTe NCs within 70 min, which is rapid when compared with the conventional refluxed method.[15]

The CdTe NCs were synthesized according to the following reaction:

$$2\mathrm{Te(NRs)} + 4\mathrm{NaBH_4} + 2\mathrm{CdL} + 7\mathrm{H_2O} \rightarrow 2\mathrm{CdTe} + 2\mathrm{H^+} + 2\mathrm{Na^+} + \mathrm{L} + \mathrm{Na_2B_4O_7} + 14\mathrm{H_2}(\uparrow)$$

where L = citrate.

Herein, Te NRs first reacted with $NaBH_4$ to generate NaHTe,[8,9,13] which would in situ react further with Cd^{2+} to form a CdTe precursor. To avoid the reduction of Cd^{2+} by $NaBH_4$, a kind of Cd complexing agent, that is, sodium citrate, was introduced before adding $NaBH_4$. On the other hand, to accelerate the reaction between Te and $NaBH_4$, Te NRs were used as the Te source.

Experimental Section

Chemicals. All of the reagents are analytically pure and used without further purification. $CdCl_2 \cdot 2.5H_2O$, Te powder, and sodium citrate were purchased from the Beijing Chemical Reagent Factory (Beijing, China). As for $NaBH_4$ and mercaptosuccinic acid (MSA), they were obtained from Aldrich.

Apparatus. The obtained products were characterized by X-ray diffraction (XRD) using a Japan Rigaku D/max-γA X-ray diffractometer with graphite-monochromatized Cu Kα radiation (k = 1.54056 Å). A scan rate of 0.02° s^{-1} was applied to record the patterns in the 2θ ranges of 20−70°. UV−vis−near-infrared (UV−vis−NIR) spectra were collected on a Cary 500 Scan UV−vis−NIR spectrophotometer. Scanning electron microscopy (SEM) images were determined with a Philips XL-30 ESEM. The accelerating voltage was 15 kV. Transmission infrared spectra were collected in the transmission mode on a Nicolet 560 FTIR spectrometer.

Preparation of t-Te Nanorods (NRs). Te NRs were prepared according to the previously published procedure with several changes.[18] Briefly, a mixture of 2 mmol of Te powder and excessive $NaBH_4$ was added successively into 2 mL of water under ambient conditions. If necessary, it can be heated to 30 °C to accelerate the reaction. During the reaction, a small outlet connected to the container was kept to open to discharge the pressure from the resulting hydrogen. After about 30 min, the resultant light-red solution was transferred into 100 mL of water under magnetic stirring. The solution immediately changed from red to black. After continuous stirring for 30 min, a black solid precipitate formed at the bottom of the flask. Finally, the resultant black precipitate was separated by discarding the upper solution, transferred into 100 mL of water, and stored under ambient conditions. To improve the dispersion of Te NRs, some surfactant such as sodium dodecyl benzenesulfonate or sodium citrate can be used to stabilize as-prepared Te NRs.[18]

Preparation of CdTe Nanocrystals (NCs). In a typical process, $CdCl_2$ (0.04 M, 4 mL), sodium citrate (0.45 g), MSA (0.11 g), the above-prepared Te NR suspension (2 mL), and excessive $NaBH_4$ (about 0.2 g) were added successively into 50 mL of water under magnetic stirring. After continuous stirring for 30 min, 12 mL of the as-obtained CdTe precursor was put into a Teflon-lined stainless-steel autoclave with a volume of 15 mL. The autoclave was maintained at 180 °C for various times to obtain CdTe NCs of different sizes. Each autoclave was cooled to room temperature via water cooling within 3 min. It should be noted that the Te suspension should be sonicated for several minutes to obtain the Te NR suspension prior to each preparation of CdTe NCs. In addition, commercial Te powders were used as the Te source instead of Te NRs at 180 °C for 45 min in a controlled experiment.

Preparation of Microtubes with Red Fluorescence. An as-prepared CdTe NC (50 mL, em = 670 nm) aqueous solution was transferred into a 100 mL conical flask. Some yellow floccules were generated via aging under ambient conditions for about 2 months. The floccules were washed with deionized water three more times to remove the free sodium citrate.

Results and Discussion

Figure 1 displays the typical evolutions of both the UV−vis absorption and the PL spectra of MSA-stabilized CdTe NCs grown at 180 °C in an aqueous solution using MSA as

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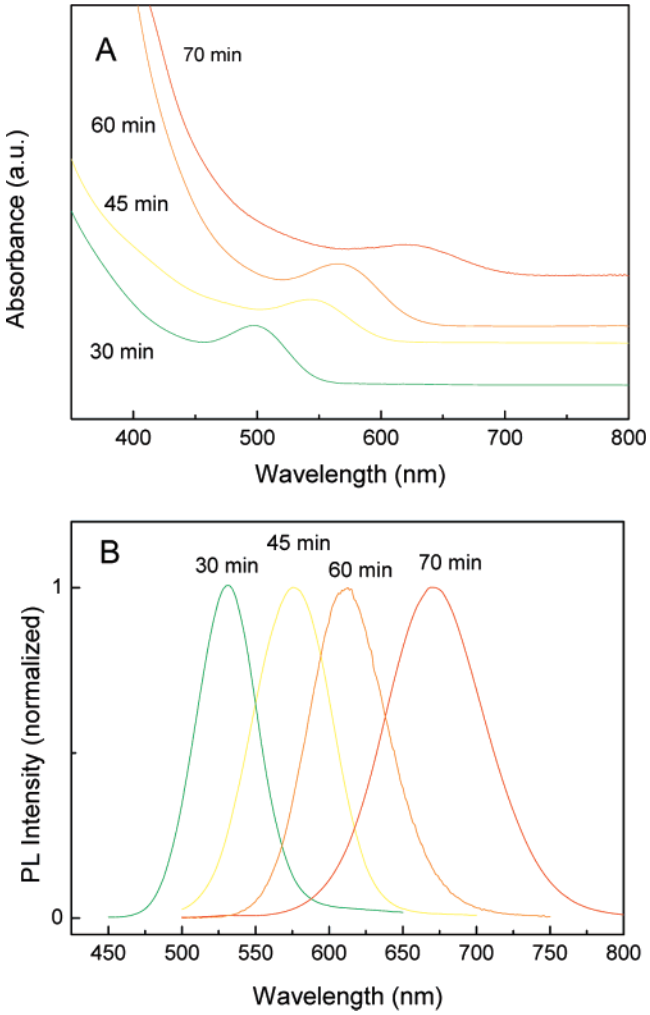

Figure 1. (A) Temporal evolution of absorption spectra of CdTe NCs grown at 180 °C stabilized by MSA. (B) PL spectra of MSA-stabilized CdTe NCs (λ_{exc} = 365 nm) grown at 180 °C for various times.

the stabilizer. As shown in Figure 1A, the color emission of CdTe NCs varies from green to red within 70 min. All of the samples reveal well-resolved absorption maxima of the first electronic transition, and the maximum shifts to longer wavelengths, prolonging the reaction time. The first excitonic transition peak position in absorption shifts from 497 to 620 nm when the reaction time was increased from 30 to 70 min. In the meantime, the PL peak position shifts from 530 to 670 nm. The relative PL QYs of the above four CdTe NCs are estimated to be 45, 30, 35, and 36%, respectively, using Rhodamine 6G as a PL reference. Although Yang et al. reported that CdTe NCs grown at 180 °C show a narrower size distribution than those grown at 100 °C, the fwhm of the PL in the present process is relatively wider compared with the results of Yang et al.,[9] which is possibly ascribed to the relatively slower reaction between Te NRs and $NaBH_4$ in comparison with the direct reaction of NaHTe and Cd^{2+}. From Figure 1B, we can see that the fwhm of the PL is about 46 nm (em = 530 nm) and increases to 80 nm (em = 670 nm), which is comparable to the quality of the former aqueous synthesis routes that used NaHTe as the Te source. For confirmation the role of Te NRs on the synthesis of high-quality CdTe NCs, a reference sample denoted as SP was made in a method similar to the method mentioned above, although instead of using Te NRs, commercial Te powder was used. As shown in Figure S3 (Suporting Information), the fluorescence of SP was too weak to detect. In addition, the fwhm (about 90 nm) was very wide in comparison with the counterpart (Te NRs as the Te source, reacting for 45 min), which may result from the relatively slow reaction between the Te powder and $NaBH_4$.

In the current hydrothermal approach, the pH value of the precursor solution was adjusted by both sodium citrate and $NaBH_4$. After the addition of $CdCl_2$ and sodium citrate, the pH value is about 7.40, which would decrease to 5.02 with the subsequent addition of MSA. It is noted that the solution is still clear without any turbidity. The pH value of the precursor solution would increase to about 9.68 after the addition of $NaBH_4$. Finally, the pH value of CdTe NC suspensions (em = 530 nm) would become 8.45. That is, with the cooperation of sodium citrate, MSA, and $NaBH_4$, the pH value of the precursor solutions could be controlled below 10. As documented by previous studies, the number of Cd^{2+}−thiol complexes on the surface of CdTe NCs, which played an important role in the enhancement of PL QYs,[19] increased remarkably with a decrease in the pH value.[21−23] Similar to the above mechanism, the lower pH value of the precursor solutions led to the relatively high PL QYs in the present route.

It is interesting that some floccules occurred from CdTe NC suspensions (em = 670 nm) after aging under ambient conditions for about 2 months. As displayed in Figure 2A, these floccules exhibited red emissions if they were excited by an UV lamp (λ_{exc} = 365 nm). The fluorescence of the above floccules was further demonstrated by a laser scanning confocal microscope. As shown in Figure 2C, these floccules are composed of wirelike morphology with red fluorescence, which have a mean diameter of about 1−2 μm and a length of up to tens of micrometers. Furthermore, scanning electron microscopy (SEM) was exploited to characterize their morphology. To observe the detailed morphology, brief sonication was applied to intentionally break some of the wirelike structure. Figure 2B indicates that they are microtubes with lengths of about several tens of micrometers and outer diameters of about 1.5 μm. In addition, the wall thickness is about 350 nm. As for their components, energy-dispersive spectrometry (EDS) and X-ray diffraction (XRD) were exploited to characterize them. From the results of EDS, we can see that the above floccules mainly contain C, O, Cd, Te, and S. As proved by Gao et al., we proposed that the S source is MSA, and S could be photochemically decomposed into S^{2-} to generate CdS via a reaction with Cd^{2+} under ambient conditions.[24,25] Figure 3B displays the XRD of the above floccules, which is similar to the results

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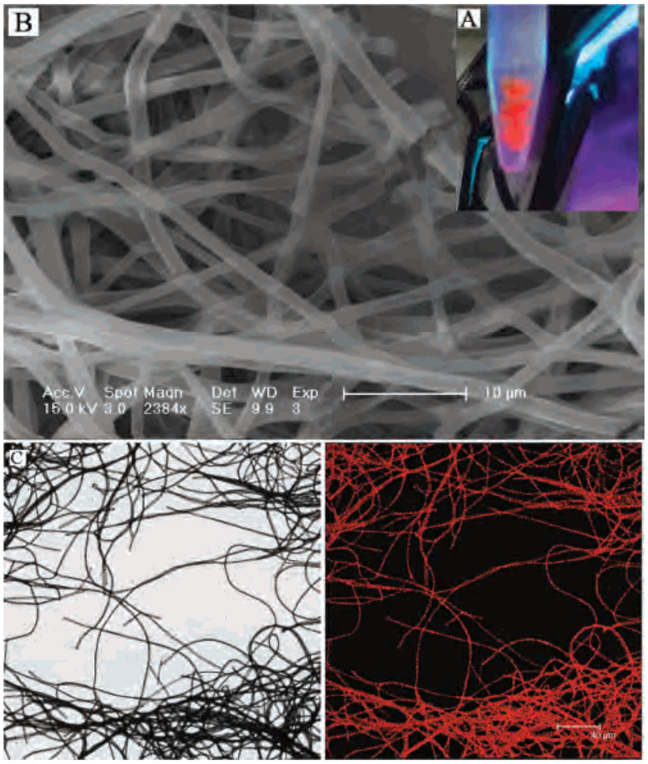

Figure 2. (A) PL image of microtubes with red fluorescence excited by a UV (λ_{exc} = 365 nm). (B) SEM images of microtubes after sonication for several minutes. (C) Confocal images of microtubes with red fluorescence under (left) bright field and (right) UV excitation (Ar, 50 mW, 405 nm).

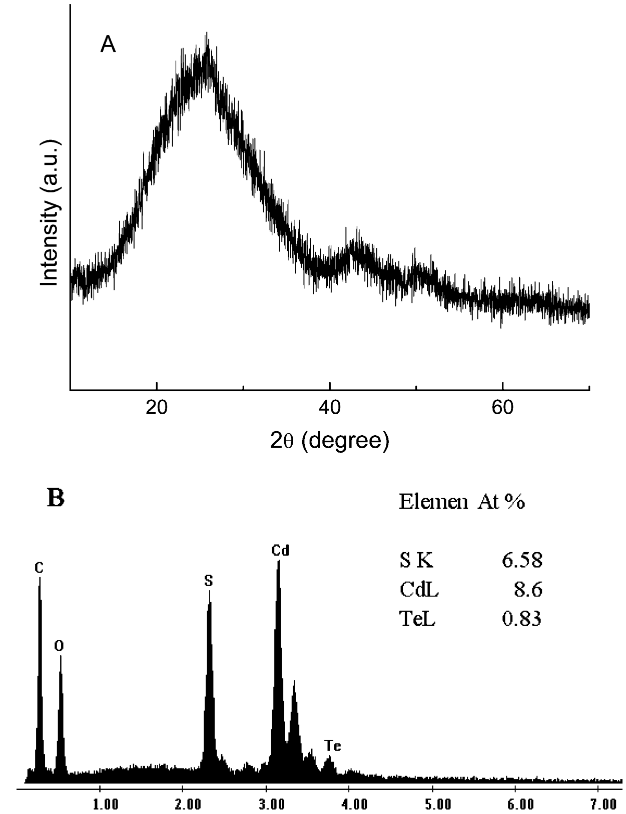

Figure 3. XRD pattern (A) and EDS (B) analysis of microtubes with red fluorescence.

of Gao et al. Because of the high ratio of S to Te in the above floccules, all of the patterns can be indexed to cubic-phase CdS. As for the source of C and O, they can be ascribed to the sodium citrate, which will be discussed later. On the basis of the above characterization, the formation process of microtubes from MSA-stabilized CdTe suspensions can be illustrated as follows. During the aging time, sodium citrate derivant (SCD) was first generated via the esterification−polymerization process of sodium citrate (Supporting Information).[26] In the meantime, MSA-capped CdTe nanoparticles spontaneously adsorbed onto the surface of 1D SCD to form CdTe microtubes, which is similar to the formation process of the tubular-morphology gold composite proposed by our group.[27] That is, a tubular-morphology gold composite could be formed via aging citrate-stabilized gold nanoparticles under ambient conditions, in which sodium citrate played the role of a template.[27] Furthermore, white floccules could be fabricated via incubation of the sodium citrate aqueous solution under ambient conditions.[26] From FTIR spectra, we can see that it is similar to sodium citrate (Supporting Information, Figure S1). Therefore, we denoted the above floccules as SCD. The results of SEM reveal that the above floccules consist of wirelike structures with diameters of around 1 μm and lengths of up to 50−100 μm (Supporting Information, Figure S2), which further demonstrate the rationality of the above formation mechanism of microtubes. As for the reason that microtubes can be generated from CdTe NC suspensions (em = 670 nm), this needs further work to investigate in detail.

Conclusion

In summary, we developed an alternative approach to the synthesis of MSA-stabilized CdTe NCs, in which Te NRs instead of unstable NaHTe were used as the Te source. Under hydrothermal conditions, the color emission of CdTe NCs could vary from green to red within 70 min. It should be noted that a complexing agent of Cd^{2+}, that is, sodium citrate, should be added to avoid the reduction of Cd^{2+} in the presence of $NaBH_4$. On the other hand, with the cooperation of sodium citrate, MSA, and $NaBH_4$, the pH value of the precursor solutions was controlled to below 10, which may have led to the relatively high PL QYs. Interestingly, microtubes with red fluorescence were spontaneously generated via aging of CdTe NC (em = 670 nm) suspensions under ambient conditions, in which SCD may serve as a template.

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Supporting Information Available: IR spectra of pure sodium citrate dihydrate, SEM image of wirelike SCD, and a PL image of CdTe NCs. This material is available free of charge via the Internet at http://pubs.acs.org.

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