Synthesis and Characterization of Wavelength-Tunable, Water-Soluble, and Near-Infrared-Emitting CdHgTe Nanorods

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One-dimensional (1D) nanostructured materials such as nanowires, nanorods, and nanotubes have drawn more attention due to both fundamental studies and high potential applications, particularly in view of technical applications.[1] Up to now, 1D nanostructures of various semiconductors have been generated in organic media mainly through decomposition of organometallic precursors at high temperatures in the presence of two or more ligands or prepared by solvothermal method.[2] The drawback of as-prepared nanocrystals mainly focuses on the fact that they are not water-soluble, which cannot be directly used in biological application. In parallel with the success of organic synthesis routes, an aqueous synthetic approach possesses many advantages, such as simplicity, low cost, controlled surface properties, and biocompatibility. However, the nanocrystals obtained in water usually possess a quasi-spherical shape.[3,4] Recently, only 1D CdTe nanomaterials prepared in aqueous media were reported.[5−10]

Size-tunable properties have become a hallmark of quantum dots (QDs) and related nanostructures.[11,12] However, the tuning of electronic, optical, and magnetic properties by changing the particle size could cause problems in many applications such as nanoelectronics, superlattice structures, and biological labeling.[14] Nevertheless, it is very important to fabricate nanomaterials with continuous tunable physical properties for nanodevice and biological application. Recent advances in ternary semiconductor nanocrystals or films have shown that their band gaps and then their optical emissions can be tuned by changing their constituent stoichiometries.[13−15] The alloyed CdHgTe nanocrystals emit in the near-infrared (near-IR) regions with tunable optical emissions, which have attracted much interest for the optoelectronics industry and therapeutics.[16] The use of nanocrystals emitting in the near-IR has been declared as the next very important step in biolabeling,[17] being especially important for medical diagnostics in blood[18] because of reduced autofluorescence background. Much effort has been spent on the synthesis of CdHgTe nanoparticles and application in cell imaging.[19−22] To the best of our knowledge, there have been few studies on the synthesis of one-dimensional water-soluble CdHgTe nanomaterials. Herein, we reported the synthesis and characterization of water-soluble CdHgTe nanorods in aqueous media.

In our experiment, CdHgTe nanorods were synthesized using CdTe nanorods as a template. First, $Cd(ClO_4)_2 \cdot 6H_2O$ and NaHTe were refluxed in water in the presence of a mixed-ligand system (thioglycolic acid (TGA) and cysteine (Cys)) to form CdTe nanorods (see the Supporting Information).[9] Different amounts of $Hg(CH_3COOH)_2$ solution were then added into the CdTe nanorods solution under vigorous stirring. The amount of Hg^{2+} ions that was added corresponded to 20, 40, and 80% of the concentration of CdTe nanorods solution that was calculated from the content of the added NaHTe.

The crystallographic properties of the as-synthesized CdHgTe nanorods were determined using powder X-ray diffraction (XRD). The XRD pattern of the as-synthesized CdHgTe nanorods was shown in Figure 1. All diffraction peaks in the pattern could be indexed to cubic-phase CdHgTe (JCPDS card 51-1122). No other impurities phase could be observed.

The morphologies of as-prepared samples with different Hg content showed little variation. Images a and b of Figure 2 showed the transmission electron microscopy (TEM) images of CdTe nanorods and CdHgTe nanorods. These two images revealed that CdHgTe nanorods preserved the shape of CdTe nanorods. The diameters of the short and the long axis of the sample remained at about 10−20 and 60−300

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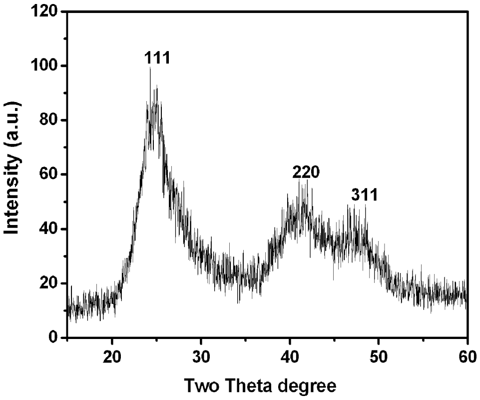

Figure 1. XRD pattern of CdHgTe nanorods.

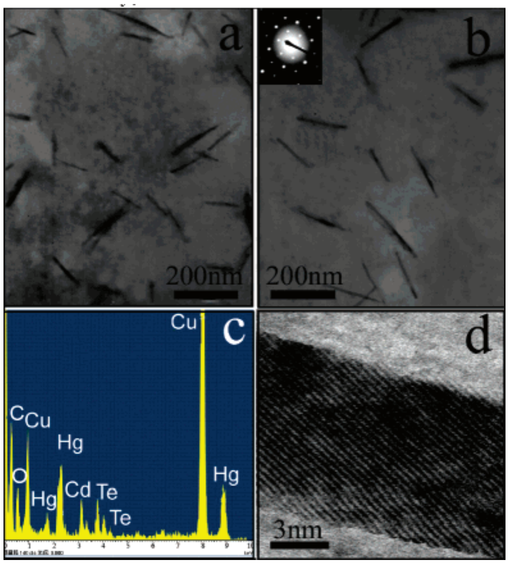

Figure 2. (a) TEM image of CdTe nanorods. (b) TEM image of CdHgTe nanorods. (c) EDS of a single CdHgTe nanorod, showing that it contained cadmium, mercury, and tellurium elements. (d) HRTEM image of a single CdHgTe nanorod.

nm, respectively, which were similar to the CdTe nanorods. The nanorods were not aggregated. The electron diffraction pattern taken from the CdHgTe nanorods was shown in Figure 2b (inset), which indicated that the nanorods had a cubic crystal structure. Figure 2d showed a typical high-resolution electron microscopy (HRTEM) image of a single CdHgTe nanorod. The interplanar spacing was about 0.321 nm, which corresponded to the (200) plane of CdHgTe nanorods. CdTe and HgTe nanomaterials with cubic crystal structure had similar crystallographic constants, which made it impossible to distinguish between CdTe and CdHgTe nanorods. However, energy disperse spectroscopy (EDS) spectra (Figure 2c) indeed showed that the nanorod contained mercury, cadmium, and tellurium elements.

With the increase in Hg^{2+} ions, the color changed from salmon pink to deep red to brown (as shown in Figure 3a–d), which showed that CdHgTe formed. This was observed experimentally as a red-shifted, in both the absorption and photoluminescence (PL) spectra. They showed the fluorescence peaks that should be red-shifted with respect to the exciton peak.[23] Panels e and f of Figure 3 showed room

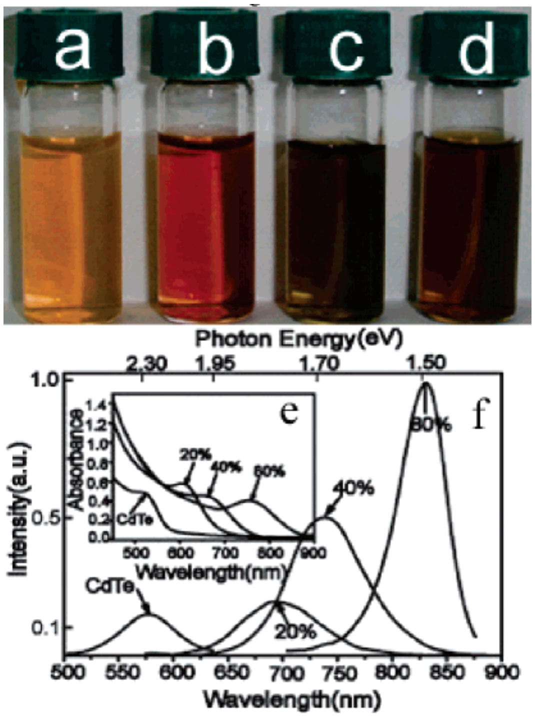

Figure 3. Photographs of aqueous solution of CdHgTe nanorods using CdTe nanorods as a template: (a) CdTe nanorods, (b) CdHg(20%)Te, (c) CdHg(40%)Te, (d) CdHg(80%)Te, (e) room-temperature optical absorption spectra of CdTe and CdHgTe nanorods, and (f) room-temperature PL spectra of CdTe and CdHgTe nanorods.

Table 1. Quantum Yield of CdHgTe Nanorods Series

samples	CdHgTe (20%)	CdHgTe (40%)	CdHgTe (80%)
QE	5.9%	9.2%	18.5%
λ_{em}	694	737	830

temperature absorption and PL of the corresponding 20-day-old CdHgTe series after purification. The samples grew in intensity significantly as the Hg-content increased and the quantum yield (QE) also increased, as shown in Table 1. In the meantime, the full width at half-maximum of fluorescence became narrower, which may be caused by the ununiformity of CdTe nanorods. When the amount of Hg^{2+} ions added was small, the ratio of HgTe to CdTe in every rod may be different because the diameter and length of CdTe nanorods were different from each other. However, when the amount of Hg^{2+} ions increased, the ratio of HgTe to CdTe in every rod inclined to be equivalent, which made the full width at half-maximum of fluorescence become narrower. The phenomenon was similar to the size effect on the full width at half-maximum of fluorescence.

The Ksp of HgTe is 20 times lower than that of CdTe. When Hg^{2+} ions were added, Cd^{2+} ions in the CdTe nanorods were substituted by Hg^{2+} ions gradually. In this synthetic system, there was a main reaction

$$\mathrm{CdTe\ (nanorods)} + Hg^{2+} \rightarrow \mathrm{CdHgTe\ (nanorods)} + Cd^{2+}$$

Both CdTe and HgTe are cubic, with $a = 6.48$ Å for CdTe (JCPDS card 15-770) and $a = 6.45$ Å for HgTe (JCPDS card 77-2014). It is difficult to distinguish them in the HRTEM image. In theory, Hg^{2+} ions would first incorporate on a surface and then into the interior of the nanorods. Figure 4 showed the contrast of fluorescence between a 3-day-old

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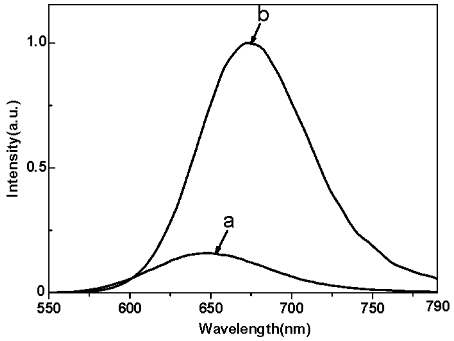

Figure 4. PL spectra of (a) 3-day-old CdHgTe nanorods and (b) 2-week-old CdHgTe nanorods.

sample and 2-week-old sample. It could be concluded that with the increased reaction time, more and more Hg^{2+} ions turned into the interior of the rods, which indicated that it was quite possible that over time the mercury content would be redistributed throughout the interior of the nanorods to form an alloy of CdHgTe.[24] The concentration of Hg^{2+} ions added in CdHgTe(80%) solution was 6.2×10^{-4} M. The content of the residual Hg^{2+} ions in the solution was 1.3×10^{-7} M determined by atomic absorbance spectrometry, which confirmed that the reaction occurred not only on the surface of the nanorods but also in the interior of the rods.

It is worth noting that the Vegard's Law for bulk and thin film alloy materials is a linear function: $E_{\mathrm{alloy}} = xE_{\mathrm{A}} + (1 - x)E_{\mathrm{B}}$, where x is the mole fraction, E_{A}, E_{B}, and E_{alloy} are the band gap energy (or other properties) of pure A, pure B, and the alloy A_xB_{1-x}, respectively. The band gap of bulk $Cd_{1-x}Hg_xTe$ alloy varies approximately linearly with composition. The band gap of HgTe nanocrystals is always smaller than that of CdTe nanocrystals.[20] CdHgTe formed with Hg^{2+} ions added into CdTe nanorods, leading to a decrease in the band gap and a shift to longer position in both the absorption and PL spectra (Figure 3). Also, the QE of HgTe nanocrystals was almost 50% at room temperature,[25] which was always bigger than that of CdTe nanocrystals. The more Hg^{2+} ions that were added, the more HgTe there was in CdHgTe nanorods, which resulted in increasing the QE.[26]

In summary, water-soluble CdHgTe nanorods were synthesized in aqueous solution. The TGA and Cys were used for solubilization. Their carboxylic group was also available for covalent coupling to various biomolecules (such as proteins, peptides, and nucleic acids) by cross-linking to reactive amine groups. Furthermore, it emitted in the near-infrared region, which was attractive for application in biolabeling, and the wavelength can be tunable with the compostion of CdHgTe nanorods. However, CdHgTe nanorods cannot be used directly for cell applications because of heavy metal toxicity. Surface coatings such as ZnS and BSA have been studied to significantly reduce cytotoxicity.[27−28]

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Supporting Information Available: The synthesis of CdTe and CdHgTe nanorods. The quantum yield determination of CdHgTe nanorods. The stability of CdHgTe nanorods. This material is available free of charge via the Internet at http://pubs.acs.org.

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