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Mixed ligand system of cysteine and thioglycolic acid assisting in the synthesis of highly luminescent water-soluble CdTe nanorods†

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Highly luminescent water-soluble CdTe nanorods were prepared with the assistance of the mixed ligand system of cysteine and thioglycolic acid; the aspect ratio and photoluminescence of the CdTe nanorods could be controlled by the refluxing time.

Nanostructured materials, especially one-dimensional (1D) materials such as nanowires, nanorods and nanotubes have been the focus of intensive research.[1–6] It is generally accepted that 1D nanostructured materials provide good systems to investigate the dependence of electrical and thermal transport or mechanical properties on dimensionality and quantum confinement.[7,8] Additionally they are also expected to play an important role as interconnects and functional units in fabricating electronic, optoelectronic and electrochemical devices with nanoscale dimensions.[9] The ability to design and generate such nanostructures is essential to modern science and technology.

CdTe is an important II–VI semiconductor material, which has been used in numerous applications, such as in light-emitting devices,[10] photoelectrochemical cells,[11,12] photonic[13] and biological labels.[14] Peng and co-workers[15] and Kumar and Nann[16] reported organometallic synthesis methods to control the morphology of CdTe nanocrystals. A solvothermal method was used to prepare 1D CdE (E = S, Se, Te) by the groups of Qian and Li.[17] However, the main disadvantage of the as-synthesized CdTe nanocrystals lies in that they are not water-soluble, which may hinder their further applications. An aqueous synthetic approach was a sophisticated route to prepare thioglycolic acid (TGA)-capped CdTe quantum dots (QDs) with many advantages, such as simplicity, high reproducibility, low cost and controllable surface properties.[18] To the best of our knowledge, this is the first report of the synthesis of highly luminescent water-soluble CdTe nanorods. Importantly, our strategy for achieving 1D growth was designed utilizing the intrinsic properties of both CdTe nanocrystals and the ligands.

In this paper, CdTe nanorods were prepared by refluxing $Cd(ClO_4)_2$ and NaHTe precursors in the presence of a mixed ligand system (TGA and cysteine (Cys)), a different approach from previous work.[18–20] The molar ratio of Cd^{2+}:TGA:Cys:HTe^- was fixed at 1:1.8:0.6:0.5. In brief, 0.0655 g of $Cd(ClO_4)_2 \cdot 6H_2O$ was dissolved in 100 ml Mill-Q water and 20 μl thioglycolic acid and 0.0152 g cysteine were added. Then the solution was adjusted to pH 11 with 1 M NaOH, and de-aerated with N_2 for 30 min. Then, 0.3 ml of oxygen-free 0.25 M NaHTe solution, which was freshly prepared from tellurium powder and $NaBH_4$ in water, was injected into the above solution under vigorous stirring. The solution was then heated and further refluxed in an oil-bath. The aspect ratios of the nanorods could be controlled by the refluxing time.

Transmission electron microscopy (TEM) images of CdTe nanorods obtained by refluxing for 1 and 3 h are shown in Fig. 1(a) and (b), respectively. The diameters of the short axis of the two samples remained at 12 nm, while the long axis changed from 57 to 134 nm on prolonging the refluxing time. The aspect ratios of the two samples were 4.75 and 11.2, respectively. The nanorods were relatively uniform. The electron diffraction pattern taken from the CdTe nanorods is shown in Fig. 1(c), which indicated that the nanorods had a cubic CdTe crystal structure. The cubic zinc blende structure also could be confirmed by X-ray diffraction patterns (XRD)[18] (see ESI, Fig. S1†). Fig. 1(d) shows a typical high-resolution electron microscopy (HREM) image of a single CdTe nanorod. The interplanar spacing was about 0.3112 nm, which corresponded to the (200) plane of the cubic CdTe. This image furthermore revealed that the structure of the nanorod was a uniform cubic CdTe crystallite.

Fig. 2 shows the photoluminescence (PL) spectra of CdTe nanorods obtained by refluxing for 1 and 3 h. The PL peaks appeared at 530 and 588 nm, respectively. As expected, the nanorods growth was accompanied by a red shift in the luminescence peaks. Since the diameter of the short axis of the CdTe nanorods was the same within experimental error, the red shift in Fig. 2(b) was due to the elongation of the long axis, *i.e.*, due to the decrease of confinement in one dimension. The full width half maxima (FWHM) of 48 and 59 nm for the 1 and 3 h samples, respectively, indicated a relative narrow size distribution.

The synthesis strategy for achieving CdTe nanorods was designed based on previous work.[20,21] After they were prepared as according to the literature,[18] the CdTe QDs were further precipi-

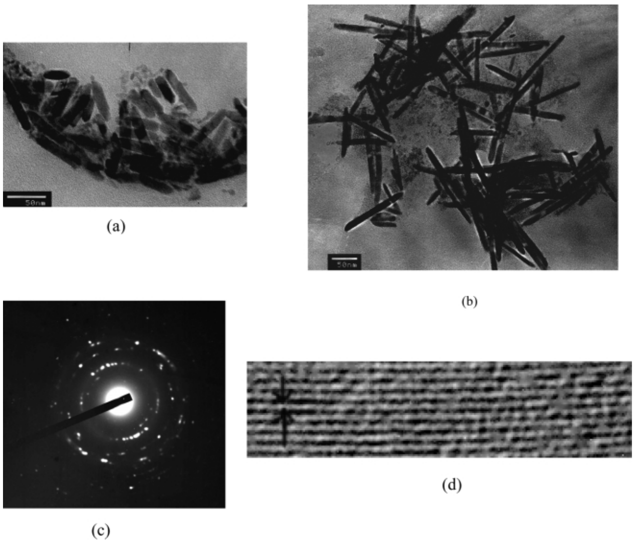

Fig. 1 TEM image of CdTe nanorods after refluxing for 1 h (a) and 3 h (b), showing that the CdTe nanorods have different aspect ratios with the change of refluxing time. Bars: 50 nm. The electron diffraction pattern of the CdTe nanorods shown in (c) were indexed as the cubic CdTe crystal structure. HREM image of a CdTe nanorod (d), showing the interplanar spacing was about 0.3112 nm. Images (c) and (d) taken from 3 h sample.

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† Electronic supplementary information (ESI) available: instrumentation, discussion of dipole attraction, XRD pattern of CdTe nanorods and TEM image of CdTe nanowires. See http://www.rsc.org/suppdata/cc/b4/b405623j/

tated by addition of isopropyl alcohol and then redissolved in pure water. The CdTe QDs could further aggregate and spontaneously organize into nanowires (TEM image of CdTe nanowires shown in the ESI†). One of the key steps in the preparation of nanowires from nanoparticles was partial removal of stabilizer (TGA), which decreased the mutual electrostatic repulsion of the nanoparticles. As a result, the dipole attraction could lead to the 1D growth when the separation between nanoparticles became short.

In the present system, the amino acid, Cys, was used as the second ligand. It is well-known that $-NH_2$ and $-COO^-$ can act as a pair of binding sites for metal ions.[22] As outlined in Scheme 1, once the small CdTe QDs formed in the reaction system, the QDs have a chance of combining with each other through the chelate function between the amino acid ligands and Cd^{2+}. The energy of the dipole attraction should assist this process, and enable the formation of CdTe nanorods. It should be emphasized that the nanorods growth orientation was confined by the lattice plane (route a) and mismatch of the lattice plane would hinder the growth in a different orientation (route b). The HREM image (Fig. 1(d)) shows that the (200) plane of the cubic crystal lattice was the predominant growth orientation. Mismatch of the lattice plane would lead to the occurrence of cross-lattice planes, none of which was observed according to the HREM images, which confirmed the growth along the one lattice plane. The existence of mixed ligands was necessary for the formation of CdTe nanorods. On the one hand, they acted as stabilizers, preventing possible aggregation and precipitation. On the other hand, they made the growth orientation more restricted, suppressing other growth directions. Although TGA or Cys have been used alone as ligands to prepare the CdTe QDs in aqueous solution, nanorods were not observed.[18,23]

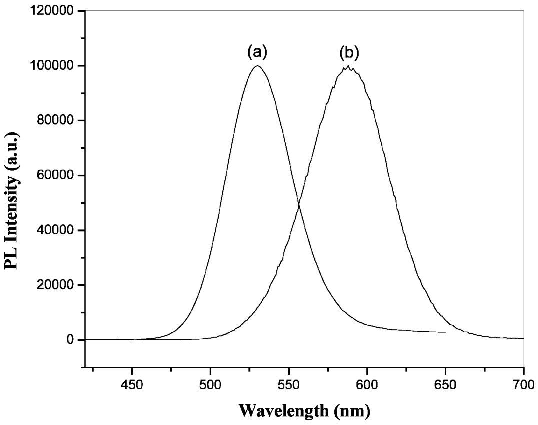
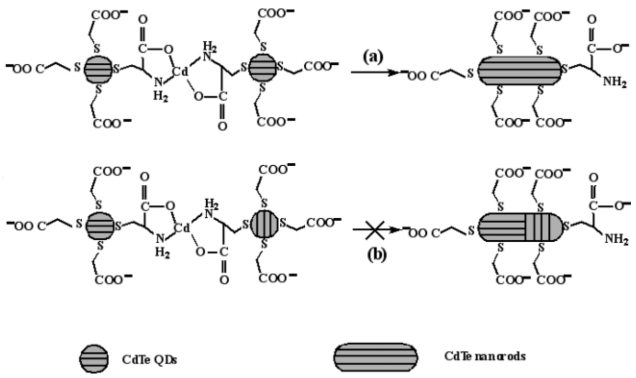


Fig. 2 PL spectra of CdTe nanorods after refluxing for 1 h (a) and 3 h (b). The excitation wavelength was 400 nm.



Scheme 1 Schematic representation of the growth process of CdTe nanorods with the assistance of the mixed ligand system of Cys and TGA. The lines in the nanorods represent the lattice plane. (a) and (b) represent the growth along matching and mismatching of lattice planes, respectively, which indicates that the 1D growth along matching lattice planes is possible while that along mismatching lattice plane is hindered.

In summary, highly luminescent water-soluble CdTe nanorods were prepared with the assistance of the mixed ligand system of amino acid (Cys) and thioglycolic acid. The aspect ratio and the PL peak could be easily controlled by the refluxing time. The dipole moment of the semiconductor and the chelate function between the amino acid ligands and transition metal ions were utilized in the strategy for achieving 1D growth, and has provided a new route for controlling construction of nanostructures, considering both of the intrinsic properties of inorganic nanocrystals and organic ligands.

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