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A facile low temperature growth of CdTe nanocrystals using novel dithiocarbamate ligands in aqueous solution

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Proline dithiocarbamic acid disodium salt (ProDTC) was first explored as a novel ligand, instead of the usual used thiols, for the synthesis of CdTe nanocrystals (NCs). Due to the weak bonding between Cd ions and ProDTC, CdTe NCs show rapid nucleation and growth at much lower temperature (30–50 °C) compared to the traditional synthesis in an aqueous solution. Moreover, faster growth of ProDTC-CdTe NCs under lower pH value was observed, while the thiol-CdTe system has an opposite tendency. The distinct growth kinetics is ascribed to the different complex constants between ProDTC-Cd and thiol-Cd, which has significant influence on the monomer activity. Although the photoluminescence quantum yield (PLQY) of as-prepared NCs was relatively low, it can be easily increased up to about 50% after further treatment of ligand exchange by replacing the surface-binding ProDTC molecules with the mercaptopropionic acid.

Introduction

Due to the unique size-dependent optical and electrical properties,¹ II–VI semiconductor nanocrystals (NCs) have attracted great attention in recent years for their potential applications in biological imaging,^{2,3} optoelectronic devices such as light emitting diodes^{4–6} and photovoltaic cells.^{7–9} Although robust and versatile techniques have been developed for high-quality II–VI semiconductor NCs synthesis, the high temperature organometallic route suffers from harsh reaction conditions such as high temperature (about 250–350 °C), the need of high vacuum to eliminate trace oxygen and the high sensitivity to the purity of the reactants.^{10–15}

The aqueous synthetic approach, as a “green” alternative, can be carried out at a much lower temperature in which water, used as the solvent, is nontoxic, inexpensive and abundant compared to organic solvents, thus facilitating the manipulation and scaling up of the synthetic process.^{16,17} Led by the pioneering work of Weller and coworkers to synthesize thiol capped II–VI NCs in aqueous solutions, great efforts have been made to improve the synthetic technique. Methods such as the hydrothermal technique^{18–20} and microwave irradiation^{21,22} have been reported to be efficient for the synthesis of high quality CdTe NCs due to the high reaction temperature and pressure. Although these methods are rapid and very useful, the extra energy has to be supplied by special equipment to satisfy the extreme conditions for the NC growth. In the industrial point of view, a low temperature synthesis in water is more favorable because facile processing, high throughput, large scale, low cost and friendly to the environment are also key factors.^{16,23–25} To

date there have been few reports on the low temperature aqueous synthesis of CdTe NCs,^{26,27} since the photoluminescence of the CdTe NCs was generally very weak due to low crystallinity and surface defect problems.^{28,29} Very recently, Liu *et al.* reported a low temperature method to synthesize CdTe NCs.³⁰ However, large amount of hydrazine hydrate was used in the reaction, which is highly toxic.

On the other hand, the nature of ligand not only influences the colloidal stability and photo-physical process of NCs,^{31–36} but also significantly concerns their growth kinetics,^{17,37–39} which is similar to the organic phase synthesis^{12,15,40–42} where the ligands bind to the surface of the growing NCs and influence the dynamic solvation of the organic–inorganic interface.⁴³ Although ligands play a crucial role in NC synthesis, the routinely used ligands are thiols such as mercaptocarboxylic acids,^{16,44–47} mercapto amines,^{43,48,49} mercapto alcohols^{16,38} and glutathione.^{50,51} To date, the research work mainly focuses on the improvement of the photoluminescence quality of thiol capped CdTe NCs rather than exploring new ligands for aqueous synthesis.^{17,52}

Recently, small molecules containing a dithiocarbamate (DTC) group (–N–C(=S)S) have gained substantial attention as the versatile and robust motifs to construct functional nanostructures by exchanging the original ligands of metal or semiconductor NCs.^{53–56} Chen and coworkers prepared silver nanoparticles by using didecylamine dithiocarbamates as the protecting ligands in an organic phase,⁵⁷ which encouraged us to explore water soluble DTCs as ligands to render the growth of CdTe NCs directly in aqueous solution as an alternative to thiol-type ligands. To the best of our knowledge, there is no report on the synthesis of II–VI NCs using DTCs as ligands neither in the organic phase nor in the aqueous phase, except for those employing DTC as a sulfur source for the synthesis of metal sulfide by single molecule thermolysis.^{58–60} Herein, we present a simple, energy saving, fast and environment friendly method to synthesize CdTe NCs by using L-proline dithiocarbamic acid

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disodium salt (ProDTC) as a new ligand in aqueous solution. Moreover, by adjusting the reaction temperature and pH value of the solution, the growth rate of CdTe NCs can be greatly altered, suggesting different growth kinetics from the thiol-stabilized CdTe NC, which is attributed to the weak bonding between ProDTC and Cd ions.

Experimental

Materials

3-Mercaptopropionic acid (MPA, 98%), 11-mercaptoundecanoic acid (MUA, 99%), tellurium powder (99.8%), CdCl₂ (99%), were purchased from Fluka and Aldrich. L-Proline, tetrahydrofuran (THF), CS₂, NaOH, ethanol, isopropanol, diether and NaBH₄ are analytical reagents from Shanghai Chemical Reagents Company. All solutions were prepared using Milli-Q water (18.2 MΩ cm, Millipore) as the solvent.

Synthesis of L-proline dithiocarbamic acid disodium salt (ProDTC)

ProDTC was synthesized according to the literature with some modifications,⁶¹ Scheme 1. Proline (5 g, 43.4 mmol) was transferred to a round bottom flask containing a solution of sodium hydroxide (3.47 g, 86.8 mmol) in a mixture of water–THF (50 ml/50 ml). The solution, cooled in an ice bath, was stirred for 30 min and then was followed by the dropwise addition of carbon disulfide (2.76 mL, 45.6 mmol). The mixture was stirred for 6 h under ambient temperature. Then the product was washed with 20 ml diether twice. The aqueous phase was collected and water was removed by a rotary evaporator. The product was dried under vacuum at 50 °C for 24 h.

Preparation of ProDTC-CdTe NCs

Briefly, the ProDTC-CdTe NCs were prepared by adding the freshly prepared NaHTe solution³⁵ to an oxygen-free CdCl₂ solution at pH 10.5 in the presence of ProDTC as ligand. The original concentrations were [Cd] = 1.25 mmol L⁻¹, [ProDTC] = 2.19 mmol L⁻¹, [NaHTe] = 0.125 mmol L⁻¹, respectively. After the NaHTe solution was injected into the CdCl₂-ProDTC solution, the reaction was carried out in a constant temperature bath and aliquots of CdTe NCs solution were taken out of the flask and cooled down to room temperature for characterization. The growth process was monitored by UV-vis and PL spectra.

Apparatus

All of the absorption and fluorescence spectra were obtained at room temperature. UV-vis absorption spectra were obtained using a Shimadzu UV-3150 UV-vis-near-infrared spectrophotometer. Fluorescence experiments were performed using Shimadzu RF-5301PC spectrofluorimeter. The PLQY of CdTe NCs

Scheme 1 Synthesis of ProDTC

was estimated by comparison with Rhodamine 6G (laser grade, Lambda Physik, QY = 95%), Rhodamine 640 (laser grade, Lambda Physik, QY = 100%), Sulforhodamine 640 (laser grade, Lambda Physik, QY = 95%) in ethanol according to the reported method, where the optical density (O.D.) of CdTe NCs at the first exciton peak and the absorption of the dye was lower than 0.1 in order to decrease the error from reabsorption.^{62–64} The PLQY of CdTe NCs was calculated using the following equation:

$$Q_s = Q_r \times \frac{I_s \times A_r \times n_s^2}{I_r \times A_s \times n_r^2}$$

where Q = quantum yield; I = integrated area of emission spectrum; A = absorbance at the excitation wavelength; n is the refractive index of the solvent; and the subscripts s and r refer to the CdTe NCs and the reference, respectively.

In order to render dispersion ability of CdTe NCs on carbon-coated copper grids before the high-resolution TEM (HRTEM, JEOL 2100F, 200kV) characterization, MUA was added to exchange the original ligands. The X-ray powder diffraction (XRD) characterization was performed on a D/max-γB diffractometer. X-Ray photoelectron spectroscopy (XPS) experiments were carried out on a RBD upgraded PHI-5000C ESCA system (Perkin Elmer) with Al Kα radiation ($h\nu$ = 1486.6 eV). Binding energies were calibrated by using the contaminant carbon (C1s = 284.6 eV). All fittings were performed using Shirley-type background and Voigt shaped peaks with an equal fwhm (full width at half-maximum) for each data set.

Results and discussion

Generally, the synthetic strategy involved the preparation of ProDTC by reacting carbon disulfide (CS₂) and L-proline in basic aqueous solution. The obtained L-proline dithiocarbamic acid disodium salts were applied as ligands to prepare a Cd-DTC aqueous solution. The Te source was generated by reducing the elemental Te powder to NaHTe using NaBH₄, which was then injected into the Cd-DTC aqueous solution with a proper pH value adjusted by a concentrated NaOH aqueous solution.

Fig. 1 shows the time course of absorption and photoluminescence spectra of CdTe NCs synthesized at 40 °C. The reaction condition for the samples was set as follows: [Cd²⁺] = 1.25 mmol, [Cd²⁺] : [ProDTC] : [HTE⁻] = 1 : 1.75 : 0.1. After the

Fig. 1 Temporal evolution of (a) UV-vis absorption and (b) PL emission (λ_{ex} = 390 nm) of CdTe NCs synthesized at 40 °C. [Cd²⁺] : [ProDTC] : [HTE⁻] = 1 : 1.75 : 0.1; pH = 10.5.

addition of NaHTE solution, an absorption shoulder located at 504 nm was detected, which is considered as a sign of nucleation of small ProDTC-CdTe clusters similar to thiol-capped CdTe NCs.^{65,66} During the fast growth process, the first electronic transition peak shifted to longer wavelength, while the intensity of the peak located at 504 nm became weaker, suggesting the formation of large particles on consumption of small clusters. The PL spectra gradually grew symmetrically and the intensity of the photoluminescence strengthened significantly. Within 5 h, the PL peak red-shifted from green-yellow (560 nm) to red region (615 nm). The full width at half maximum (fwhm) of the NC ensemble during the growth was *ca.* 34–38 nm which is comparable to that synthesized with the traditional aqueous synthesis.

Low temperature growth of ProDTC-CdTe NCs

Though 40 °C is lower than the reaction temperature in the traditional aqueous method, even lower growth temperature could also be adopted. As shown in Fig. 2(a), after the growth of CdTe NCs at 30 °C for 5 h, the PL emission peak reached 583 nm. But only about 1 h was needed if the growth took place at 50 °C, which is much faster than the traditional aqueous synthesis. As known, the adhesion energy attaching and detaching of the ligands on the NC surface greatly influences the growth process.^{43,67} According to the Arrhenius equation, lower activation energy leads to a higher reaction rate, so it is reasonable to infer that the activation energy of DTC-CdTe is smaller than that of thiol-CdTe. In the situation in our approach, the values of stability constant ($\log\beta_2$) of Cd-DTC complex is between 11–12,^{68,69} while $\log\beta_2$ of Cd-thiol complex is between 16–17,^{39,70} indicating that the Cd-thiol complex is much more stable. It also confirms that the former has a smaller activation energy. Fig. 2(b) reveals that the PLQY increased from about 4% to 16%, when the reaction temperature increased from 30 °C to 50 °C. However, a fast drop of PLQY was concomitant at higher reaction temperature which may originate from the weak chemical stability of the ProDTC-Cd complex, resulting in the poor passivation of surface defects of CdTe NCs.

Fig. 2 Temporal evolution of (a) PL peak ($\lambda_{ex} = 390$ nm) and (b) PLQY of CdTe NCs synthesized at different temperature, with $[Cd^{2+}] : [ProDTC] : [HTE^-] = 1 : 1.75 : 0.1$, pH = 10.5.

Fig. 3 Temporal evolution of (a) PL peak ($\lambda_{ex} = 390$ nm) and (b) PLQY of CdTe NCs with various DTC-to-Cd molar ratios, $[Cd^{2+}] : [HTE^-] = 1 : 0.1$, pH = 10.5, $T = 40$ °C.

Comparison of the growth and PLQY of CdTe NCs at different ProDTC-to-Cd ratios

As shown in Fig. 3, ProDTC-to-Cd molar ratio plays an important role in both the growth rate and PLQY of CdTe NCs. By reducing the ligand concentration, the growth rate significantly increases. However, when $[ProDTC] : [Cd]$ is lower than 1.5, the aggregation of CdTe NCs was observed during the growth procedure, owing to the lack of sufficient repulsion force between CdTe NCs provided by the $-COO^-$ groups of the ligands absorbed on the CdTe NC surface. Meanwhile, the increase of ProDTC-to-Cd molar ratio not only reduces the growth rate but also weakens the PL intensity, which is similar to the thiol-stabilized CdTe NCs.^{17,39} As reported, although ProDTC ligands can act as useful stabilizers, the photoluminescence was also quenched for the core-only CdSe NCs.⁵⁴ When different amounts of ProDTC were added into the as-prepared CdTe NCs solution, the PL intensity decreased gradually with increasing the quantity of ProDTC (data not shown), which also gives evidence that the low PL intensity is not due to the lack of ProDTC ligands on the surface but the quenching from the ProDTC molecules. Taking the conflict between colloidal stability and PLQY into account, the optimized ProDTC-to-Cd molar ratio is 1.75 at which both the growth rate and PL intensity are relatively high, and the aggregation of CdTe NCs is also avoided.

The influence of pH

To investigate the influence of pH on the growth of CdTe NCs, a series of CdTe NCs were prepared by fixing $[Cd^{2+}] = 1.25$ mmol L^{-1} , $[Cd^{2+}] : [ProDTC] : [HTE^-] = 1 : 1.75 : 0.1$, while the pH value was altered from 9.5 to 11.5. This pH range was chosen because when the pH value is lower than 9.5 precipitation may happen during the growth and when the pH value is higher than 12 the precursor solution may be turbid sometimes. As shown in Fig. 4(a), the ProDTC-capped CdTe NCs grow much faster at lower pH. The emission peak of NCs prepared at pH 11.5 was at 558 nm, while that at pH 10.0 red-shifted to 624 nm. However, the thiol-capped CdTe NCs prepared in aqueous solutions have an opposite tendency,^{17,39,71} indicating that the pH value plays

Fig. 4 Temporal evolution of (a) PL peak ($\lambda_{\text{ex}} = 390 \text{ nm}$) and (b) PLQY of CdTe NCs growth at various pH values, with $[\text{Cd}^{2+}] : [\text{ProDTC}] : [\text{HTe}^-] = 1 : 1.75 : 0.1$, reaction temperature was set as 40°C .

different roles in the two systems. As reported previously, during the preparation of Cd-TGA or Cd-MPA solution, a white precipitate, also known as neutral mono thiolates (CdL), gradually dissolves when NaOH solution is added to increase the pH value. Thus, OH^- can increase the solubility of CdL which was proposed responsible for the quick growth of CdTe NCs at high pH.^{18,71} However, in the case of ProDTC-CdTe, white precipitate was not observed unless the pH value was increased to more than 12. In order to get more information about the composite, XPS characterization was performed on the precipitate from the ProDTC-Cd precursor solution at pH = 12.5 and a MPA-CdTe sample was used for comparison. The O/C atomic ratio of the MPA-CdTe sample calculated from XPS experimental is 0.67, very near the theoretical value 0.69 (assuming the C, O elements of the sample all originating from the ligands on the NCs surface). However, the experimental O/C atomic ratio of the precipitate from the ProDTC-Cd precursor solution is 1.72, about five times the one of the ProDTC-Cd complex, which suggests that complexation between OH^- and Cd^{2+} may compete with that of ProDTC-Cd and form some $\text{Cd}(\text{OH})_2$ -like compounds. As known, dithiocarbamates can form 1 : 1 and 1 : 2 complexes with Cd^{2+} ions similar to a thiol-Cd complex, but their stability constants are much smaller as discussed above. In the 1 : 2 complex, Cd-ProDTC has a stability constant $\log\beta_2$ of 8.33.^{68,69,72} When the pH was increased to 12.5, the molar ratio of OH^- to ProDTC increased to about 16, which may shift the chemical equilibrium to form more $\text{Cd}(\text{OH})_2$ and reduces the concentration of Cd-ProDTC monomers, resulting in the slow growth of CdTe NCs. Fig. 4(b) shows that the PLQY decreased when pH is higher or lower than 10.5. Combined with the discussion above, at higher pH value OH^- may interfere with the complexation between Cd^{2+} and ProDTC and reduce the growth rate of CdTe NCs, which eventually leads to introducing more defects and decreasing the PLQY of CdTe NCs.

PL enhancement by adding MPA

As mentioned above, the low activation energy allows CdTe NCs to grow at lower temperature. Therefore, it is essential to stop the growth when CdTe NCs reach the desired PL peak. Because

thiols are much stronger ligands for Cd^{2+} ions as shown in the former discussion, MPA was chosen to stop the growth by partially or fully replacing the ProDTC molecules absorbed on the CdTe surface. As shown in Fig. 5(a) and (b), after the addition of an equal molar amount of MPA relative to the Cd^{2+} ions ($n_{\text{MPA}} = n_{\text{Cd}}$) in the ProDTC-CdTe NCs solution (pH 10.5), a 3 nm blue-shift of the absorption peak appeared and prolonging the stirring time cannot lead to further change of the absorption peak, which may be seen as a sign of the successful ligand exchange. Surprisingly, the PL intensity of CdTe NCs increased significantly as shown in Fig. 5(c). The PLQY of three different CdTe NCs synthesized at 30, 40 and 50°C , respectively, can be enhanced up to 23%, 33% and 47% from 5%, 7% and 15%, respectively. The blue shift of the absorption peak and PL enhancement may originate from two possible ways. (1) During the ligand exchange process, S ions were released either from the DTC or MPA, and then substituted Te atoms on the NCs' surface, thus the CdS shell formed and the actual CdTe core shrunk. Therefore, a blue shift appeared and the PL intensity increased due to the elimination of the defects. (2) Before MPA was added into CdTe NC solution, there existed a rough ProDTC-Cd ligand shell with various defects. When MPA, a much stronger ligand for Cd^{2+} ions, is introduced into the solution, the fragile ligand shell is removed and the size of CdTe NCs reduced slightly. Consequently, a dense thiolate complex shell which acts as a wide-bandgap material to confine the exciton inside the CdTe core formed and nonradiative recombination is depressed. The key between the two possibilities is

Fig. 5 The change of (a) UV-vis spectra and (b) PL spectra after the ligands exchange with MPA at 40°C . (c) The enhancement of photoluminescence after adding MPA to the as-prepared CdTe NCs synthesized at 30°C (III), 40°C (II) and 50°C (I), respectively. (d) Photograph of CdTe NCs with different sizes taken under UV light.

whether S ions are incorporated into the CdTe lattice and forms CdS shell. In order to get more information from the surface structure of CdTe NCs after ligand exchange, XPS was used to obtain the core level binding energy of S 2p. As known, the S 2p peaks can be fitted by constraining the difference of S 2p_{3/2} and S 2p_{1/2} at 1.2 eV and the peak areas with a ratio of 2 due to the spin-orbit splitting. As shown in Fig. 6, after ligand exchange, the S 2p spectrum of CdTe NCs can be well fitted with a single doublet with S 2p_{1/2} peak at 163.1 eV and S 2p_{3/2} at 161.9 eV, which is consistent with that of Cd-thiolates.^{73–75} This result reveals that the surface of CdTe NCs is a Cd-MPA complex shell formed in the ligand exchange process and rather than a CdS shell, which is also supported by XRD characterization discussed later. Also we tried to perform the XPS characterization on ProDTC-CdTe NCs without ligand exchange for contrast. However, due to the weak coordination of the ProDTC to Cd²⁺, the CdTe NCs solution turned dark and became turbid during concentration though under reduced pressure and at a low temperature (40 °C). After being precipitated by adding isopropanol the obtained solid was black and the PL was almost quenched when redispersed in water, which suggests that the ProDTC-capped CdTe NCs seems unstable during the sample post-treatments. The XPS results (data not shown) revealed that there exists two S 2p_{3/2} peaks: the one located at 168.2 eV can be assigned to sulfur oxide and the other located at 161.2 eV originates from CdS.⁷⁶ Based on the above results we emphasize the importance of the ligand exchange by MPA for preserving both the stability and PL intensity of as-prepared CdTe NCs.

Fig. 7(a) shows an XRD pattern of CdTe NCs synthesized at 40 °C. The intensity and position of the three strongest diffraction peaks match well with the CdTe cubic structure rather than the CdS cubic structure. Previous reports mentioned that the incorporation of sulfur from thiol ligands into the growing CdTe NCs^{16,42} shifts the diffraction peaks to larger angles. However, no obvious deviation of XRD reflexes can be found here, which gives another evidence that the CdTe NCs

Fig. 6 XPS spectra of CdTe NCs after ligand exchange with MPA for S 2p core level.

Fig. 7 (a) Powder XRD pattern of CdTe NCs after ligand exchange with MPA. It shows the cubic CdTe and CdS reflections with their relative intensities. (b) High resolution transmission electron microscope (HRTEM) image of CdTe NCs after ligand exchange with MPA.

prepared by our method are not CdTeS alloy. HRTEM was used to characterize the structure of the CdTe NCs. As shown in Fig. 7(b), the NCs are quasi-spherical particles with average diameter about 3.5 nm. The existence of well resolved lattice planes in the inset of Fig. 7(b) demonstrates the high crystallinity of the nanocrystals.

In summary, ProDTC, as one of the representative dithiocarbamates, has been successfully exploited to synthesize CdTe NCs in aqueous solution. Rapid growth of CdTe NCs at low temperature is distinct from thiol-capped CdTe NCs, which is attributed to the low stability of the ProDTC-Cd complex. After exchanging the original ligands of as-prepared ProDTC-CdTe NCs by simply adding MPA, the PLQY can be improved up to almost 50%. The low-temperature growth characteristics of ProDTC-capped CdTe NCs demonstrates that DTCs are novel model compounds to moderate the growth of II–VI NCs in aqueous solution. The further investigation of how the ligand affects the growth of CdTe NCs is ongoing in our lab.

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