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One-Pot Synthesis of Dual-Stabilizer-Capped CdTe Nanocrystals with Efficient Near-Infrared Photoluminescence and Electrochemiluminescence

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CdTe nanocrystals (NCs) are promising near-infrared (NIR) emitter candidates. A one-pot synthetic strategy has been developed for high-quality NIR-emitting CdTe NCs with mercaptopropionic acid and sodium hexametaphosphate as dual stabilizers. The dual-stabilizer-capped CdTe NCs displayed efficient photoluminescence (PL) between the visible and near-infrared region (533–778 nm) with a quantum yield of up to 47 %. XRD, XPS, and photoluminescence spectra were employed to characterize the structure and optical features of these samples. Moreover, the NIR-emitting CdTe NCs also displayed strong band-gap electrochemiluminescence in the NIR region, indicating that this strategy can be used to synthesize NCs with both efficient fluorescence and electrochemiluminescence emissions in the NIR region.

Introduction

Semiconductor nanocrystals (NCs), often referred to as quantum dots (QDs), are promising fluorescent lumophores.[1,2] NCs with photoluminescence (PL) in the near-infrared (NIR) window, especially between 650 and 900 nm, are of particular interest for their possible sensing application since the auto-fluorescence and absorption from biological tissues are lowest in this spectral window.[3–5] Even though high-quality NIR-emitting NCs are usually achieved with multistep high-temperature organometallic approaches,[6] synthesizing NIR-emitting NCs in aqueous solution is arousing much attention.[7–9]

CdTe is an important small-band-gap material, and water-soluble visible-emitting CdTe NCs have been extensively prepared in aqueous media.[2] Because type-II NCs can demonstrate a longer PL wavelength than any of the single materials,[10,11] a large amount of aqueous synthetic methods have been carried out for type-II CdTe NCs including CdTe-based core/shell systems,[10] or alloys.[12] Although several type-II NIR-emitting CdTe NCs, such as CdTe/CdS,[13] CdTe/CdSe,[14] CdTe/ZnS,[15] CdHgTe,[16] and CdHgTe/CdS[17] have been synthesized, this strategy is still extremely challenging. Firstly, a pretreatment to synthesize the unstable Te sources (H_2Te or NaHTe) is needed, and a Schlenk line is required. Secondly, type-II CdTe NCs are relatively complicated and usually involve multistep processes, i.e., the core of NCs is first synthesized and then capped with a thin shell of other reactants.[18] Thirdly, the high toxicity and poor stability of the Hg-based alloyed CdTe NCs is unfavorable in bio-applications.[17] Finally, despite a few examples of NIR-emitting CdTe NCs having been demonstrated,[7,19] the PL quantum yields (QY) in the NIR window are usually less than 10 %.[20]

Although a one-pot synthetic strategy has obvious advantages in preparing NIR-emitting NCs,[9] less work has been carried out for NIR-emitting CdTe NCs with this strategy. This is probably because of the low PLQY of visible-emitting CdTe NCs prepared with the one-pot strategy.[21] In this manuscript, with mercaptopropionic acid (MPA) and sodium hexametaphosphate (HMP) as dual stabilizers, a one-pot strategy for high-quality water-soluble NIR-emitting CdTe NCs has been developed. This strategy is more facile and environmentally friendly than the aqueous synthetic approaches with a Schlenk line, as it can be carried out in an open-air aqueous environment. More importantly, the NIR-emitting CdTe NCs display strong band-gap electrochemiluminescence (ECL) in the NIR region, so that the ECL spectrum can be directly recorded with a normal florescent instrument, which indicates an efficient new ECL emitter in the NIR region. This one-pot synthetic strategy is capable of synthesizing CdTe NCs with varied optical applications.

Results and Discussion

Synthesis of Water-Soluble, NIR-Emitting CdTe QDs and the Reaction Conditions

The detailed synthetic steps are described in the Experimental Section. After sodium tellurite (Na_2TeO_3) was added to a cadmium chloride solution in the presence of

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HMP and MPA, the initial solution turned pale yellow and then gradually became a rich yellow with refluxing, indicating the complex binding between Cd^{2+} and TeO_3^{2-}. In this case, HMP not only acted as a capping agent, but also as a dispersing agent to prevent the deposition of cadmium tellurite ($CdTeO_3$). After hydrazine hydrate had been introduced, the initial solution rapidly turned to red, indicating that CdTe NCs were achieved upon reducing TeO_3^{2-} to Te^{2-} by hydrazine hydrate. Figure 1 displays the temporal absorption and PL spectra of CdTe NCs in a typical synthetic process. Both absorption and emission spectra shifted to longer wavelengths with prolonged refluxing time, as expected on the basis of the "quantum-confined size effect". All samples displayed well-resolved first electronic transition peaks in the absorbance spectra and a narrow full width at half maximum (FWHM) in the PL spectra, indicating a narrow size distribution of the as-prepared CdTe NCs. On the basis of the sizing curve for aqueous synthesized thiol-capped CdTe NCs,[7] the diameter of the NCs in Figure 1 was determined to be around (a) 2.3 (b) 2.5 (c) 2.8 (d) 3.2 (e) 3.7 (f) 4.4 (g) 5.1 and (h) 5.5 nm. Although the tellurite compound[21–23] and hydrazine hydrate[24] have been extensively used for the synthesis of CdTe NCs, these results are the first to provide a one-pot strategy to synthesize high-quality water-soluble CdTe NCs with a PL emission in the NIR region. Compared with previous synthetic methods for NIR-emitting CdTe NCs, this one-pot strategy has the advantage of simplicity, being environmentally friendly, and dispensing with the preparation of an unstable Te precursor.

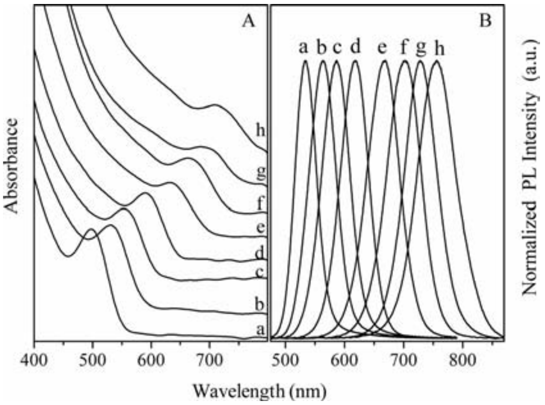

Figure 1. (A) Absorption and (B) PL spectra of CdTe NCs recorded after particle growth for (a) 10, (b) 30, (c) 60, (d) 120, (e) 480, (f) 600, (g) 840, and (h) 1200 min.

The effects of the MPA stabilizer on the PL of the CdTe NCs are shown in Figure 2. Although a higher molar ratio of MPA to Cd^{2+} at the initial stage tends to slow down the growth rate of CdTe NCs, PL spectra with an FWHM range from 40 to 84 nm (Figure 2B) are obviously narrower than those of NIR InAs/ZnSe NCs (about 77–85 nm),[25] Cu–In–Se NCs (about 100 nm),[26] and NAC-capped CdTe/CdS (about 62–97 nm)[13] within similar emission ranges. A relatively higher PLQY beyond 10% in the NIR region was obtained with a varied molar ratio of MPA/Cd^{2+}, and the highest PLQY of up to 47% was achieved at 560 nm with a molar ratio of MPA/Cd^{2+} of 3:1. The formation of a black precipitate with a molar ratio of Cd^{2+}/MPA of 1:0 indicated that HMP on its own cannot result in CdTe NCs.

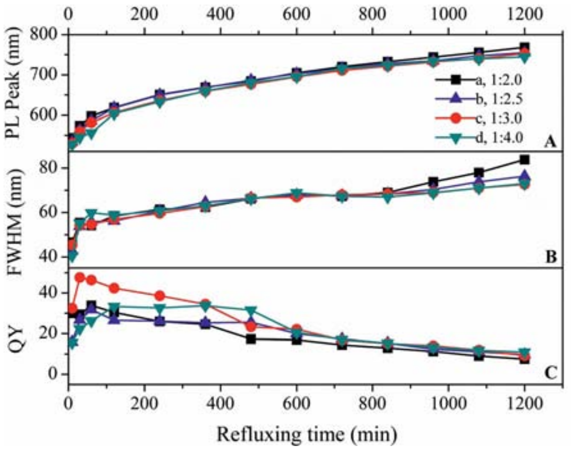

Figure 2. Effects of MPA on (A) PL peak position, (B) FWHM, and (C) QY of the as-prepared NCs with the molar ratio of Cd^{2+}/MPA being (a) 1:2.0, (b) 1:2.5, (c) 1:3.0, and (d) 1:4.0.

The other stabilizer, HMP, also displayed important effects on the PL features of CdTe NCs (Figure S1, Supporting Information). CdTe NCs with a tunable PL and narrow FWHM were achieved with a varied molar ratio of Cd^{2+}/HMP between 1:0.7 and 1:2.8. When the molar ratio of Cd^{2+}/HMP was 1:0, a much wider FWHM and lowered PLQY were obtained, indicating that MPA on its own also failed to result in high-quality CdTe NCs. Since the binding site at the surface of the CdTe NCs for HMP and RS– can be exchanged by adjusting the concentration ratio,[27] and since competitive binding behaviors of MPA and HMP towards Cd^{2+} ions at the surface of the CdTe NCs result in improved PL emission,[28] it is the dual stabilizers that play an important role in the high quality of the CdTe NCs.

The effects of the precursor Na_2TeO_3 were explored with varied molar ratios of Na_2TeO_3 to Cd^{2+} (Figure 3). Although a higher molar ratio of Na_2TeO_3/Cd^{2+} could broaden the PL FWHM and lower the PLQY, a tunable PL emission with an FWHM of less than 80 nm and a PLQY beyond 10% in the NIR region were achieved with a molar ratio range between 0.05:1 and 0.25:1 (Figure 3B, C). In conventional synthesis procedures, tellurium powder or tellurite chemicals were reduced by strongly reducing sodium borohydride to NaHTe or H_2Te.[8,21,29] $N_2H_4 \cdot H_2O$ is a weak reductant even under refluxing conditions; thus, the reduction process for TeO_3^{2-} to Te^{2-} was much slower than that of sodium borohydride.[21] As the slow generation of Te^{2-} was favorable for nucleation processes of CdTe NCs, high-quality CdTe NCs were achieved with the use of the dual stabilizers. With a decreased amount of hydrazine, the growth rates of the NCs decreased dramatically (Figure S2 and S3 of the Supporting Information), which might indicate that Ostwald ripening may be avoided by adjusting the initial reaction conditions.

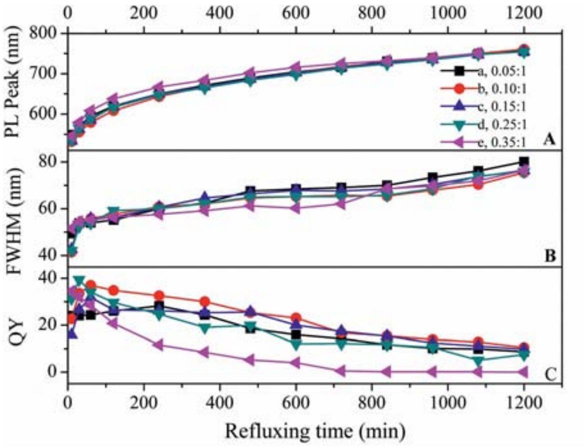

Figure 3. Effects of Na_2TeO_3 on (A) the PL peak position, (B) FWHM, and (C) QY of the as-prepared NCs with a molar ratio of Te/Cd^{2+} of (a) 0.05:1, (b) 0.10:1, (c) 0.15:1 (d) 0.25:1, and (e) 0.35:1.

The following chemical reactions [Equations (1) and (2)] are proposed for the synthesis processes:

$$3\ N_2H_4 \cdot H_2O + 2\ TeO_3^{2-} \rightarrow 3\ N_2\uparrow + 9\ H_2O + 2\ Te^{2-} \quad (1)$$

$$CdL + Te^{2-} \rightarrow CdTe + L;\ L = MPA \quad (2)$$

In an aqueous synthetic strategy with unstable NaHTe or H_2Te as the Te sources, an alkaline initial solution is usually required,[8] as the formation of cadmium–thiol complexes strongly depends on the initial acidity of the solution.[29] However, CdTe NCs with tunable PL could easily be achieved with a wide acidity range between pH = 5.5 and 12.0 by this one-pot strategy, as shown in Figure 4. The narrow PL spectra (less than 80 nm, Figure 4B) and desirable NIR PLQY (Figure 4C) can easily be achieved within a wide range of pH values between 8.0 and 12.0. Thus, this one-pot strategy is capable of synthesizing CdTe QDs with a wide acidity range.

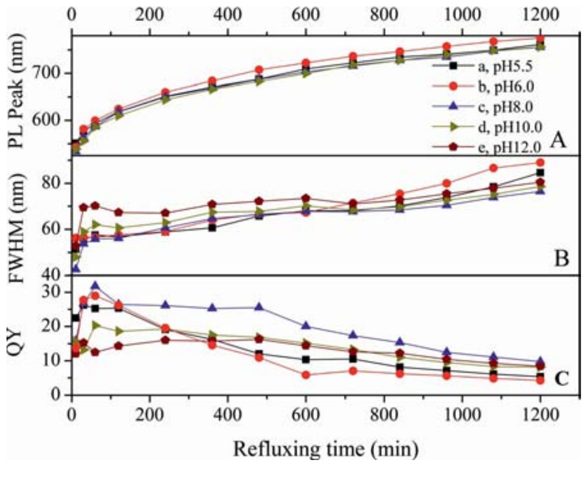

Figure 4. Effects of the solution acidity on (A) the PL peak position, (B) PL FWHM, and (C) QY of the as-prepared NCs with pH values of (a) 5.5, (b) 6.0, (c) 8.0, (d) 10.0, and (e) 12.0.

Structural Properties of the CdTe NCs

Sample (f) in Figure 1 was used to characterize the structure of the as-prepared CdTe NCs. A powder X-ray diffraction (XRD) analysis of the sample displayed broad peaks at 2θ values of 25.2°, 41.5°, and 48.9°, corresponding to the (111), (220), and (311) planes of cubic CdTe, as shown in Figure 5.[24] The broadness of the peaks was attributed to the small dimensions of the CdTe NCs. The shift of reflections toward the position corresponding to cubic CdS resulted from the existence of Cd–S bonds between cadmium ions and thiols on the surface of the NCs,[7] which was further proven by the binding energies of 158.9 and 159.8 eV for the typical $S_{2p1/2}$ and $S_{2p3/2}$ peaks of S_{2p}[30] in a corresponding XPS spectrum, as shown in Figure 6. As a typical stabilizer for the synthesis of the II–VI and III–V NCs in aqueous media,[31] HMP can compete with thiols for complexation with the Cd^{2+} ions.[28] The binding energies of 129.5 eV for P_{2p} provided unambiguous evidence that the stabilizer HMP also binds to the Cd^{2+} ions at the surface of the CdTe NCs. The binding energies of 402.4 and 570.0 eV for Cd_{3d} and Te_{3d}, respectively, proved that CdTe NCs are achieved by this one-pot synthetic strategy. The molar ratio of Cd/Te/S/P atoms at the NC surface was detected as 47.12:7.22:24.69:20.97. Although commercial HMP normally consists of polyphosphate with a chain

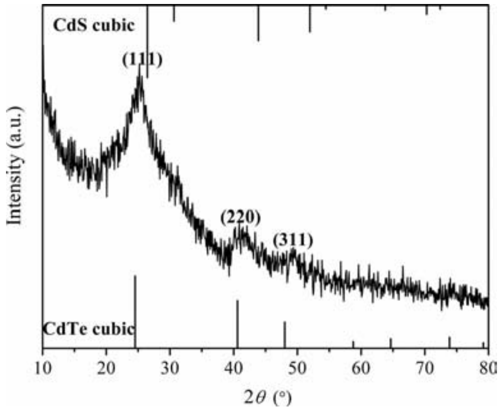

Figure 5. XRD patterns of CdTe NCs.

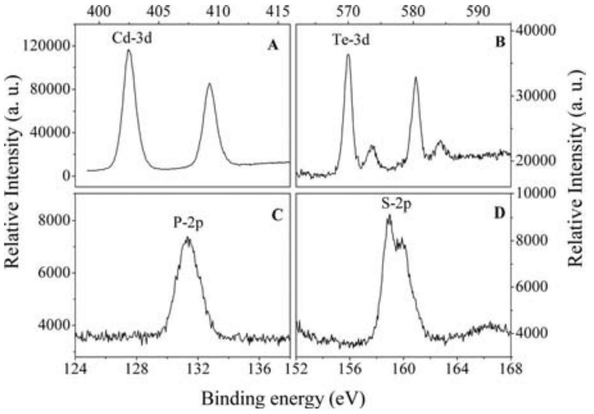

Figure 6. XPS of CdTe NCs.

length of up to 450 (PO_3) units, the molar ratio of Cd/Te/MPA/HMP at the surface of the NCs was found to be 47.12:7.22:24.69:3.50 corresponding to the formula of $(NaPO_3)_6$ for HMP. These results not only provided further evidence that the CdTe NCs were capped with dual stabilizers, but also manifested the core/shell NCs posses many surface traps, since the binding sites for HMP at the NCs surface can result in an imperfected CdS shell.

Strong Band-Gap ECL Emission of CdTe NCs in the NIR Region

The as-prepared NCs also displayed strong band-gap ECL emissions in the NIR region. As shown in Figure 7, sample (f) with a PL emission at 703 nm (as shown in Figure 1) was chosen for the ECL measurement; an intensive anodic ECL emission from the NCs at 0.95 V was observed for pH = 8.0 PBS with tri-*n*-propylamine (TPrA) as the coreactant. More importantly, the ECL transient of the same CdTe NCs [inset (A)] was greatly enhanced at 0.95 V with prolonged time, so that the ECL spectrum could be obtained with a common florescent instrument, shown in inset (B). During the ECL transient measurement, the ECL emission appeared immediately upon onset of the potential, suggesting that the ECL response of the CdTe NCs was very quick. The ECL spectrum was much closer to the PL spectrum of the NCs (Figure 1f), suggesting a band-gap NIR ECL emission from the as-prepared CdTe NCs. It is well known that traditional ECL emission is usually located over the visible range, such as Luminol (ca. 420 nm) and $Ru(bpy)_3^{2+}$ (ca. 620 nm). The strong band-gap ECL emission from the as-prepared CdTe NCs not only indicated a new ECL emitter in the NIR region, but also made it possible for multiple ECL sensing of the NCs. Further explorations concerning the ECL feature of the as-prepared CdTe NCs and their possible applications are being carried out.

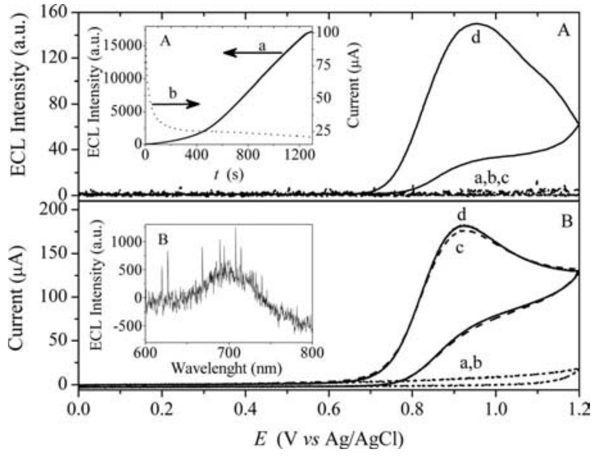

Figure 7. (A) ECL and (B) electrochemical behavior of (a) 0.1 mol/L pH = 8.0 PBS (b) containing 0.20 μmol/L NCs, (c) 10.0 mmol/L TPrA, and (d) 10.0 mmol/L TPrA + 0.20 μmol/L NCs. Scan rate: 50 mV/s. Inset: ECL transients of 0.20 μmol/L CdTe NCs in 0.1 mol/L PBS containing 10.0 mmol/L TPrA at a potential of 0.95 V [curve (a) of inset (A)], corresponding chronoamperometric curve [curve (b) of inset (A)] and spectrum (B).

Conclusions

We have developed a facile dual-stabilizer approach for the aqueous synthesis of CdTe NCs with emissions up to the near-infrared region. The as-prepared CdTe NCs not only displayed outstanding PL features, such as narrow PL FWHM, a wide emitting range from 533 to 778 nm, a high PLQY of up to 47%, and good storage stability for two months, but also exhibited strong band-gap NIR electrochemiluminescence, indicating that CdTe NCs prepared by this strategy can be used as novel ECL emitters in the NIR region. Moreover, high-quality CdTe NCs can easily be achieved under varied reaction conditions, such as various concentrations of the precursors and initial acidity of the solution.

Experimental Section

Materials and Chemicals: All chemicals used in the experiments were of analytical grade or the highest purity grade (commercially available) and used without further purification. MPA was obtained from Aldrich Chemicals. Na_2TeO_3 was obtained from Shanghai Jingchun reagent Co., Ltd. (Shanghai, China). Rhodamine 6G was obtained from Acros Organics (NJ, USA). HMP was obtained from GuangCheng Chemical Co., Ltd. (Tianjin, China). Hydrazine hydrate was obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All solutions were prepared with doubly distilled water.

One-Pot Synthesis of Dual-Stabilizer-Capped CdTe NCs: For a typical synthesis, a cadmium chloride solution (1.6 mL, $CdCl_2$: 0.10 mol/L) was added to a three-necked flask containing H_2O (50 mL). HMP (293.6 mg) and MPA (34.6 μL) were then added successively under magnetic stirring. After the solution pH was adjusted to 8.0 by adding NaOH (1.0 mol/L) dropwise, Na_2TeO_3 (5.3 mg) was added to the above solution, and the crude material turned to green-yellow immediately. After the resulting mixture was refluxed at 100 °C for 10 min, $N_2H_4 \cdot H_2O$ (2.4 mL) was injected into the above solution, and then the final solution was refluxed under open-air conditions. The final molar ratio of HMP/Cd^{2+}/Te/MPA/$N_2H_4 \cdot H_2O$ was 2.1:1:0.15:2.5:260. Aliquots of the sample were taken at different time intervals and used to record UV/Vis and PL spectra without any postpreparative treatment. The obtained crude products were precipitated three times by acetone with centrifugation at 12000 rpm for 10 min, and the resultant precipitates were redissolved in doubly distilled water of the same volume for the other characterizations.

Instrumentation and Characterization: Absorption spectra were obtained by using a TU 1901 UV/Vis spectrophotometer (Beijing, China). PL and ECL spectra were recorded with a WGY-10 spectrofluorimeter (Tianjin, China). The QY of CdTe NCs was determined by using Rhodamine 6G in ethanol (QY = 95%) as the PL reference.[32] XRD patterns were recorded with a Bruker AXS D8 Advance X-ray diffractometer with Cu-K_α radiation (λ = 1.5418 Å). X-ray photoelectron spectra (XPS) were obtained with a *K*-Alpha X-ray photoelectron spectrometer (Thermo Fisher Scientific Co., USA). Cyclic voltammetry and ECL were carried out with an MPI-A multifunctional electrochemical and chemiluminescent system (Xi'an Remex Analytical Instrument Ltd. Co., China) with a configuration consisting of a glassy carbon working electrode (5.0 mm in diameter), an Ag/AgCl (saturated KCl) reference electrode and a platinum counter electrode. The ECL spectrum was directly recorded with a WGY-10 spectrofluorimeter (Tianjin, China) by chronoamperometric triggering ECL emission at 0.95 V.

Supporting Information (see footnote on the first page of this article): Effects of sodium hexametaphosphate and hydrazine hydrate on the optical features of CdTe quantum dots.

Acknowledgments

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