Facile synthesis and application of highly luminescent CdTe quantum dots with an electrogenerated precursor†

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An electrogenerated precursor has been developed for green synthesis of highly luminescent aqueous CdTe quantum dots (QDs) with unique quantum yield and strong electrogenerated luminescence, which can access cellular targets via specific binding and have potential application as biosensors in highly sensitive biosensing and cell imaging.

CdTe quantum dots (QDs) are currently attracting enthusiastic interest due to their unique size-dependent optical and electrical properties for potential application in optoelectronics and biolabeling. However, the low quantum yield (QY) and difficult synthesis of aqueous CdTe QDs are hindering their application in biological imaging10 and detection.10 Up to now three types of tellurium sources, Te powders,2–3 Al2Te3 lumps4 and TeO2–5.6 have been used for the synthesis of CdTe. Te powders, the most popular source, must first be dissolved in high-boiling-point solvents for nonaqueous synthesis,10 or slowly reduced by NaBH4 to NaHTeac2b or reacted with ammonia and aluminium to give (NH2)2Tea2 for aqueous synthesis under an inert atmosphere. When humidity-sensitive Al2Te3 lumps are used as a source of NaHTe, the synthesis has to be performed with a Schlenk line.24 Although TeO2–5 as an alternative Te source can be reduced for preparing CdTe film5 or nanowire arrays6 by electrodeposition of self-controlled atomic layer epitaxy, the products cannot be converted to luminescent CdTe QDs.

Herein, we report a facile synthesis of highly luminescent CdTe QDs in an aqueous system with a novel Te source to conveniently produce a CdTe precursor using a cathodic stripping Te electrode. The versatility of the present protocol has been validated by preparing CdTe QDs with different functional groups using mercaptoacetic acid (MAA) and N-acetylcysteine (ACYS) as stabilizers. The luminescent behaviors of as-prepared QDs investigated by photoluminescence (PL) and electrogenerated luminescence (ECL) show their potential application in optical and ECL biosensing with high sensitivity. The as-prepared CdTe QDs were successfully labeled to antibody for access to cellular targets for cell imaging.

The Te disc electrode for cathodic stripping was prepared by sealing a Te rod (4 mm in diameter) in a glass tube. The generation of the Te precursor was carried out using an applied potential of −1.05 V in the electrolyte containing 2.0 mM Cd2+ and 4.8 mM MAA at pH 11 adjusted with 0.05 M NaOH solution. The reduction potential of [Cd(MAA)]2+ was calculated to be −1.11 V from the equilibrium constant of [Cd(MAA)]2+, thus this applied potential could avoid the deposition of Cd on the electrode (ESI†). The CdTe precursor could be easily formed due to the favorable thermodynamics3 in the presence of MAA at pH 11, accompanied by a color change of the electrolyte from colorless to yellow and finally to dark brown. The amount of Te precursor was controlled by adjusting the charge consumed during cathodic stripping according to Faraday’s law. Subsequently, the solution of CdTe precursor was heated in a water bath at 80 °C under stirring, and CdTe QDs were gradually crystallized. The size of the QDs could be controlled by changing the heating time, which was monitored by UV–Vis absorption with Peng’s empirical equations.8

The molar ratio of Cd to Te greatly affected the luminescent behaviors of CdTe QDs at the same heating time, which could be measured by inductively coupled plasma (ESI†). The optimal molar ratio of Cd to Te occurred at 1 : 0.4, at which the obtained QDs showed the strongest PL emission. As shown in Fig. 1 and ESI† for MAA and ACYS stabilizers, all UV–Vis spectra showed well-resolved maximum absorption of the first electronic transition, indicating a sufficiently narrow size distribution of the QDs. The results were also confirmed from the PL spectra with a FWHM less than 44 nm.

**Fig. 1** UV–Vis absorption (a) and PL spectra (b) of MAA-capped CdTe QDs obtained at different heating times. The absorption peaks occur at 495, 506, 534, 547, 558 and 565 nm, and the PL emission peaks are at 530, 537, 562, 578, 598 and 609 nm (λex = 388 nm) for the heating times of 1, 2, 6, 8, 14 and 20 h, respectively. The inset in (a) shows fluorescent photographs of as-prepared CdTe QDs under UV irradiation.
The fluorescent color under UV irradiation changed from green to yellow, orange and finally red with increasing heating time (inset in Fig. 1a). The red-shifts of the color, the absorption edge and the maximum PL emission wavelength indicated the growth of CdTe QDs during the heating treatment. The sizes of the QDs could be estimated from the UV–Vis absorption spectrum by Peng’s empirical equations to be from 2.0 to 3.5 nm. This indicated that the size of the QDs could be tuned simply by varying the heating time in the bath. The PL emission intensity also depended on the heating time (Fig. 1b). With the increase of heating time from 0.5 h to 6 h, the PL emission intensity increased due to the improvement of the crystallization and annealing effect of defects, and the maximum PL emission occurred at 6 h. This result was different from that observed previously and could be explained in terms of the mechanism of Ostwald ripening and defocusing. However, further heating resulted in a decrease in PL emission intensity due to broad distribution and relatively small surface/volume ratio of the obtained QDs.

The UV–Vis absorption and PL spectra of QDs obtained from different synthesis batches showed close positions of absorption and emission peaks, and the same sharp shapes, indicating the similar size and good reproducibility of these as-prepared QDs.

With increasing heating time the QY of PL emission increased markedly. The changes were different for MAA- and ACYS-capped QDs (ESI†). The QY of MAA-capped CdTe QDs increased from 10.8% to 63.8% as the heating time was prolonged from 0.5 h to 8 h and then reached a maximum value of 77.3% at 20 h. The QY of ACYS-capped CdTe QDs also increased markedly from 12.1% at 0.5 h to a maximum value of 79.0% at 8 h. Further heating resulted in a slight decrease of QY. Such a remarkable QY is comparable with that reported for nonaqueous CdTe QDs (70%), and much higher than those of CdTe QDs with aqueous synthesis. The luminescence efficiency was stable during the storage of the CdTe crystallites at 4 °C over several months. These results indicate that the as-synthesized CdTe QDs have high QY and favorable stability. Thus, the proposed method to electrogenerate the precursor was efficient for the synthesis of highly luminescent CdTe QDs. The excellent photophysical behavior of QDs allowed fine-tuning to select discrete emission and excitation properties for biolabeling and imaging applications.

The morphology of the CdTe QDs was characterized with high-resolution transmission electron microscopy (HRTEM). It showed the lattice fringes of the particles with an average size of 3.2 nm (Fig. 2a), indicating a highly crystalline structure of CdTe. The average size was consistent with the result obtained from the UV–Vis absorption. The predominance of edged rhombohedral and tetrahedral crystallites seen from the HRTEM image indicated that the shape of the QDs could not be considered as near spherical. The Fourier transform pattern of the selected area further confirmed the short-range ordering crystallinity of these as-prepared QDs (Fig. 2b).

The heating time for obtaining CdTe QDs showed less influence on the interplanar distances. The HRTEM image showed interplanar distances of 3.57 and 2.13 Å in two directions (Fig. 2a), corresponding to those of 3.52 and 2.12 Å for CdTe in a hexagonal primitive-type structure (JCPDS 190193), which could not present in a cubic face-centered or orthorhombic primitive structure. The present CdTe QDs exhibited a structure different to that of cubic zinc blende described in previous reports. The dense accumulation of hexagonal primitive could be the structural origin of highly luminescent CdTe. As seen from Fig. 2c, the powder X-ray diffraction (XRD) spectrum showed a strong diffraction peak at the center of 2θ. Several sharp diffraction peaks at the 2θ values of around 26.7° and 43.9° possibly came from the CdS phase in a hexagonal primitive type structure (JCPDS 010783), which was formed between MAA and the surface of the CdTe to result in a core–shell heterostructure, and usually found in mercapto-capped QDs. In contrast, no phase of Cd(OH)₂, such as hexagonal primitive (JCPDS 730969), monoclinic end-centered (JCPDS 712137) or x-Cd(OH)₂ (JCPDS 120062), was observed in the powder XRD spectrum, indicating there was no hydroxide on the surface of the particles.

Information on the surface energy of the CdTe QDs could be obtained from their ECL behaviors. Fig. 3 shows the cyclic voltammograms (curve 1) and ECL curve (curve 2) of MAA-capped CdTe QDs solution on a glassy carbon electrode. Three small reduction peaks were observed at −0.43, −0.85 and −1.33 V, while two oxidation peaks appeared at −0.61 and +0.95 V, respectively. These cathodic peaks can be attributed to the reduction of Cd elements, CdTe and CdS phase, and atomic Te from the CdS phase in a hexagonal primitive type structure. The oxidation peaks resulted from the oxidation of the reduced state of Cd and the injection of holes in the 1S₀ quantum-confined orbital of the CdTe core, respectively.

Upon the potential scan a cathodic ECL peak was observed at −0.61 V, which was 1.24 V more positive than that of the cathodic

![Fig. 2](image1.png)

**Fig. 2** HRTEM image (a), Fourier transform pattern of the selected area (b) and powder XRD spectrum (c) of MAA-capped CdTe QDs obtained on heating for 6 h.

![Fig. 3](image2.png)

**Fig. 3** Cyclic voltammograms (curve 1) and ECL curve (curve 2) of MAA-capped CdTe QDs solution on heating for 6 h on a glassy carbon electrode at a scan rate of 0.1 V s⁻¹ in 0.1 M KCl as supporting electrolyte.
ECL emission of CdTe nanoparticles in organic media. This emission cannot be explained by annihilation between redox species of QDs due to the absence of the oxidized species of QDs as electron acceptors. One possibility is that the emitter was produced by other oxidized species as coreactants from the supporting electrolyte or impurities. Meanwhile, the ECL produced by other oxidized species as coreactants from the holes-injected QDs and reduced species. The electrochemical ECL emission can be attributed to an annihilation process between the holes-injected QDs and reduced species. The anodic ECL emission curve showed a strong anodic emission at +1.26 V. The anodic ECL emission cannot be explained by annihilation between redox species of QDs due to the absence of the oxidized species of QDs and reduced species. The electrochemical band gap between the two ECL peaks was 1.87 eV, which was less than that of 2.21 eV (562 nm) from PL emission peaks. This could be because the two ECL peaks are located at potentials inside the valence band edge for electron and hole injections into the surface traps of the particles. The strong ECL behaviors further confirm the high luminescence and the potential ECL biosensing application of CdTe QDs synthesized with the electrogenerated precursor.

To verify the benefits of the as-prepared CdTe QDs, the MAA-capped CdTe QDs were employed to label a major histocompatibility complex class II (MHC-II) antibody for cell imaging. The avidin was conjugated to MAA-capped QDs via electrostatic self-assembly. After removing the excess avidin with an ultracentrifuge filter (MWCO 100,000 g mol$^{-1}$), the conjugates were coupled with anti-MHC-II via an avidin bridge and then used for bioimaging the skeleton of mouse peritoneal macrophage. The nonspecific binding was effectively blocked by 1% bovine serum albumin (BSA). Fig. 4 shows the confocal micrograph of peritoneal macrophage from mouse incubated with CdTe QDs-labeled anti-MHC-II at 25 ± 1 °C, which is distributed in cytoplasm surrounding the nuclei. The CdTe QDs-labeled anti-MHC-II could specifically bind to cytoplasm immunogen of peritoneal macrophage. The accessibility of QDs labeled antibody to MHC-II in a cellular matrix illustrated the feasibility of using QDs for biological tugging and cell imaging.

In summary, an electrogenerated precursor is designed firstly for facile synthesis of highly luminescent CdTe QDs in aqueous solution with ecological safety, cost-efficiency, humidity insensitivity, and favorable reproducibility. The obtained CdTe QDs have good crystallizability, favorable monodispersity, high QY, strong anodic ECL emission and good stability. The present approach can be widely used in the preparation of CdTe capped with different surface stabilizers or other telluride QDs. Moreover, CdTe QDs can access cellular targets and stain the fine features such as the cell nucleus; they have potential application as biological labels in sensitive biosensing and cell imaging.

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Notes and references

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Facile synthesis and application of highly luminescent CdTe quantum dots with an electrogenerated precursor

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Experimental

Materials. mercaptoacetic acid (MAA), N-acetyl-cysteine and cadmium chloride hemipentahydrate were purchased from ACROS and used without further purification. Tellurium rods were donated by Leshan Kaiyada photoelectricity Co. (China). All other chemicals were of analytical grade and used as received. Water with the conductivity of 18 MΩ cm was used in the whole experiment and all solutions were thoroughly deaerated by bubbling with nitrogen.

Apparatus. UV-vis absorption and photoluminescence (PL) spectra were recorded at room temperature with an UV-3600 spectrophotometer (Shimadzu Co.) and a F900 fluorescence spectrometer (Edinburgh Instruments Ltd., UK), respectively. Rhodamine B with a PL quantum yield (QY) of 89% was used as a standard for determining the room-temperature PL quantum yields of CdTe QDs following the previously reported procedure.\textsuperscript{S1}

The structure and composition of the as-prepared CdTe QDs were characterized with powder X-ray diffraction analysis with Co K\(\alpha\) radiation and accelerating voltage of 45 kV (XRD, Shimadzu XRD-6000) and high-resolution transmission electron microscopy (HRTEM, JEM-2100, JEOL) coupled with electron diffraction. Compositional analysis of Cd and Te was performed with inductively coupled plasma-atomic
emission spectrometer (ICP-AES, Jarrell-Ash, J-A1100). The confocal micrograph was obtained on TCS-SP2 (Leica) laser scanning confocal microscope.

The electrochemical measurements and electrogenerated precursor for one-pot synthesis of Te precursor for one-pot synthesis were performed on CHI 660B workstation (American CH Instrument Co., Austin, TX) with a three-electrode system composed of glassy carbon or Te electrode as the working, Ag/AgCl/KCl (sat.) (+0.22 V vs NHS) as reference and platinum wire as counter electrodes. The ECL experiments were carried out on a MPI-A multifunctional electrochemiluminescence analytical system (Xi’an Remex Electronic & Technological Co., China) with glassy carbon working electrode. The ECL emission was detected with a model BPCL ultraweak chemiluminescence analyzer (Institute of Biophysics, China) in a pulse mode at 800 V, which was sensitive to photons with a wavelength range of 200-800 nm.

Cyclic voltammograms of Cd\(^{2+}\) in absence and presence of MAA

The standard electrode potential of Cd\(^{2+}/0\) is -0.403 V (vs NHS).\(^{S2}\)

Cd\(^{2+}\) + 2e \rightleftharpoons Cd\(^0\) \hspace{1cm} (1)

At pH 11 Cd\(^{2+}\) species is in the form of hydroxyl complex\(^{S3}\) with a log\(\beta\) value of 8.65:\(^{S4}\)

Cd\(^{2+}\) + 4OH\(^-\) \rightleftharpoons [Cd(OH)\(_4\)]\(^2-\) \hspace{1cm} (2)

The reduction potential of [Cd(OH)\(_4\)]\(^2-\)/Cd\(^0\) is obtained from eqs (1) and (2) and the log\(\beta\) value to be -0.46 V (vs NHS), equivalent to -0.68 V (vs Ag/AgCl). After 4.8 mM MAA was injected into 2.0 mM CdCl\(_2\) solution at pH 11 to form [Cd(MAA)\(_3\)]\(^4-\) with a log\(\beta\) value of 19.11,\(^{S4}\)

[Cd(OH)\(_4\)]\(^2-\) +3MAA\(^2-\) \rightleftharpoons [Cd(MAA)\(_3\)]\(^4-\) + 4OH\(^-\) \hspace{1cm} (3)

the electrode reaction for [Cd(MAA)\(_3\)]\(^4-\) can be expressed as follows:

[Cd(MAA)\(_3\)]\(^4-\)+2e \rightleftharpoons Cd + 3MAA\(^2-\) \hspace{1cm} (4)

Thus the reduction potential of [Cd(MAA)\(_3\)]\(^4-\)/Cd\(^0\) can be calculated to be -1.11 V (vs Ag/AgCl).
The cyclic voltammogram of CdCl₂ in 0.1 M KCl (pH 11) at glassy carbon electrode showed a reduction peak potential of -0.81 V (curve 1, Fig. S1a), which was 0.13 V more negative than the theoretic value due to the presence of reduction overpotential at glassy carbon electrode. Upon addition of 4.8 mM MAA, both the reduction and anodic stripping peaks disappeared, no obvious reduction of [Cd(MAA)₃]⁴⁻ was observed at the potentials more positive -1.2 V (curve 2, Fig. S1a), indicating a reduction overpotential of larger than 0.09 V, identical to the result observed at curve 1. Thus no reduction deposition of [Cd(MAA)₃]⁴⁻ occurred at the potentials more positive than -1.2 V.

![Cyclic voltammograms of 2.0 mM CdCl₂ in 0.1 M KCl (pH 11) in (1) absence and (2) presence of 4.8 mM MAA on glassy carbon (a) and Te (b) electrodes. Scan rate: 50 mV s⁻¹. Curve 0 was obtained in the blank electrolyte.](image)

**Fig. S1.** Cyclic voltammograms of 2.0 mM CdCl₂ in 0.1 M KCl (pH 11) in (1) absence and (2) presence of 4.8 mM MAA on glassy carbon (a) and Te (b) electrodes. Scan rate: 50 mV s⁻¹. Curve 0 was obtained in the blank electrolyte.

Fig. S1b depicts the cyclic voltammogram of CdCl₂ in 0.1 M KCl (pH 11) at Te electrode in absence and presence of 4.8 mM MAA. In blank 0.1 M KCl solution the Te electrode showed a cathodic wave with an onset potential of -0.93 V (curve 0, Fig. S1b) and a peak occurred at -1.21 V, which was not observed at the glassy carbon electrode, indicating the stripping of Te to Te²⁻, which has a formal potential of -1.16 V (vs Ag/AgCl).⁵⁵

\[
\text{Te}^0 + 2e \longrightarrow \text{Te}^{2-} \quad (5)
\]

During the back sweep, a small anodic peak was observed due to the oxidation of Te²⁻ to Te at the potential of -0.89 V. It indicated that only a fraction of Te²⁻ was oxidized to Te due to the diffusion of...
produced Te$^{2-}$ to solution. When CdCl$_2$ was added to the solution, the cyclic voltammogram showed the same reduction curve of Te to Te$^{2-}$, and one reduction of Cd$^{2+}$ could also be observed at the potential around –0.45 V (curve 1, Fig. S1b), which disappeared after 4.8 mM MAA was added (curve 2, Fig. S1b), as observed at glassy carbon electrode. Compared with curve 1, the increase of anodic wave on curve 2 was possibly due to the oxidation of formed CdTe QDs at Te electrode, which could take place at glassy carbon electrode, as shown in Fig. 4. From these results the optimal applied potential for electrogeneration of Te precursor in one-pot synthesis of CdTe QDs could be selected at –1.05 V (vs Ag/AgCl), which could avoid the electroposition of Cd.

**Schematic depiction on facile synthesis of CdTe QDs**

Typically, the electrolyte was prepared by dissolving cadmium chloride hemipentahydrate (22.9 mg, 100 µmol), MAA (18 µL, 240 µmol) and potassium chloride (373 mg, 5 mmol) in 50 mL ultrapure water. The pH was adjusted with 0.05 M solution of NaOH. The molar ratio of Cd$^{2+}$ to capping agent was 1:2.4, which had been used in the earlier stage of CdTe QDs preparation (ref. 2-4). The facile synthesis of CdTe QDs was based on cathodic stripping of Te electrode using an applied potential of -1.05 V in as-prepared electrolyte with a three-electrode system. The amount of Te precursor was controlled with the charge consumed during cathodic stripping according to Farady’s law. Subsequently, the solution of CdTe precursor was heated on a water bath at 80 °C under stirring and CdTe QDs were gradually crystallized. The heating time of precursor controlled the desired size of QDs, which was monitored by UV-Vis absorption with Peng’s empirical equations. Finally, the formed CdTe colloid was dialyzed exhaustively against water overnight at room temperature to obtain CdTe QDs solution. The schematic depiction on the synthesis of CdTe QDs was shown in Fig. S2.
**Fig. S2.** Schematic depiction on one-pot synthesis of CdTe QDs with cathodic tellurium electrode in presence of MAA.

**Effect of molar ratio of Cd to Te on luminescent behavior**

The PL spectra of CdTe QDs obtained at different amounts of Te precursor with heating duration of 6 h were shown in Fig. S3. The molar ratios of Cd to Te greatly affected both the maximum intensity of PL emission and the peak position. The optimal molar ratio of Cd to Te occurred at 1:0.4 with a strongest PL emission at 562 nm.

**Fig. S3.** PL spectra of MAA-capped CdTe QDs with different ratios of Cd to Te. The PL intensities are 179.8 (1:0.2), 252.4 (1:0.4), 131.6 (1:0.6), 95.2 (1:0.8) and 24.3 (1:1), respectively. Excitation wavelength: 388 nm.
**UV-Vis absorption and PL spectra of ACYS-capped CdTe QDs**

All UV-Vis absorption spectra of ACYS stabilized CdTe QDs obtained with different heating times showed well-resolved maximum absorption of the first electronic transition (Fig. S4a). With the increasing heating time the maximum absorption wavelength showed a red-shift from 482 nm (0.5 h) to 578 nm (20 h), while the PL emission wavelength also red-shifted (Fig. S4b) and the fluorescent color under UV irradiation changed from green to yellow, orange and finally red (inset in Fig. S4a). The PL emission intensity increased with the increasing heating duration from 0.5 h to 10 h, and then greatly decreased and maintained at low emission intensity. The red-shift of the maximum absorption wavelength and PL emission wavelength was due to the increasing size of QDs, while the increasing PL emission intensity was due to the improvement of the crystallization and annealing effect of defects. The decrease of the PL intensity after 10 h resulted from the low concentration, large size and relatively small surface-to-volume ratio of the obtained QDs.

![Fig. S4. UV-Vis absorption (a) and PL (b) spectra of ACYS-capped CdTe QDs obtained with different heating durations. The absorption peaks occur at 482, 499, 512, 525, 532, 540, 547 and 578 nm for 0.5, 2, 4, 8, 10, 12, 14 and 20 h, respectively, while the PL emission peaks occur at 532, 541, 547, 557, 562, 565, 577 and 609 nm, respectively ($\lambda_{ex} = 388$ nm). Inset in (a): fluorescence photographs of as-prepared CdTe under UV radiation.](image-url)
Dependence of size and QY of MAA and ACYS-capped QDs on heating time

With the increasing heating time the sizes of both MAA and ACYS-capped CdTe QDs increased and trended to the maximum values, and their QYs showed different changes (Fig. S5). The QY of MAA-capped CdTe QDs increased from 10.8% (at 0.5 h) to 63.8% (at 8 h) and then trended a maximum value. The QY reached 77.3% at 20 h. The QY of ACYS-capped CdTe QDs increased agilely from 12.1% at 0.5 h to the maximum value of 79.0% at 8 h. The further increasing heating duration resulted in the decrease of QY.

Fig. S5. Comparison of diameter (a) and quantum yield (b) evolution profiles for MAA-stabilized (■) and ACYS—stabilized(○) CdTe QDs with heating durations at 80°C.

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