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

Cunwang Ge, Min Xu, Jing Liu, Jianping Lei, and Huangxian Ju*

Key Laboratory of Analytical Chemistry for Life Science (Education Ministry of China),
Department of Chemistry, Nanjing University, Nanjing 210093, and Department of
Chemistry, Nantong University, Nantong 226007, P.R. China

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.[S1]

The structure and composition of the as-prepared CdTe QDs were characterized with powder X-ray diffraction analysis with Co Kα 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]

$$Cd^{2+} + 2e \longrightarrow Cd^0 \qquad (1)$$

At pH 11 Cd^{2+} species is in the form of hydroxyl complex[S3] with a logβ value of 8.65:[S4]

$$Cd^{2+} + 4OH^- \rightleftharpoons [Cd(OH)_4]^{2-} \qquad (2)$$

The reduction potential of $[Cd(OH)_4]^{2-}/Cd^0$ is obtained from eqs (1) and (2) and the logβ 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 logβ value of 19.11,[S4]

$$[Cd(OH)_4]^{2-} + 3MAA^{2-} \rightleftharpoons [Cd(MAA)_3]^{4-} + 4OH^- \qquad (3)$$

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

$$[Cd(MAA)_3]^{4-} + 2e \rightleftharpoons Cd + 3MAA^{2-} \qquad (4)$$

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 $CdCl_2$ 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.

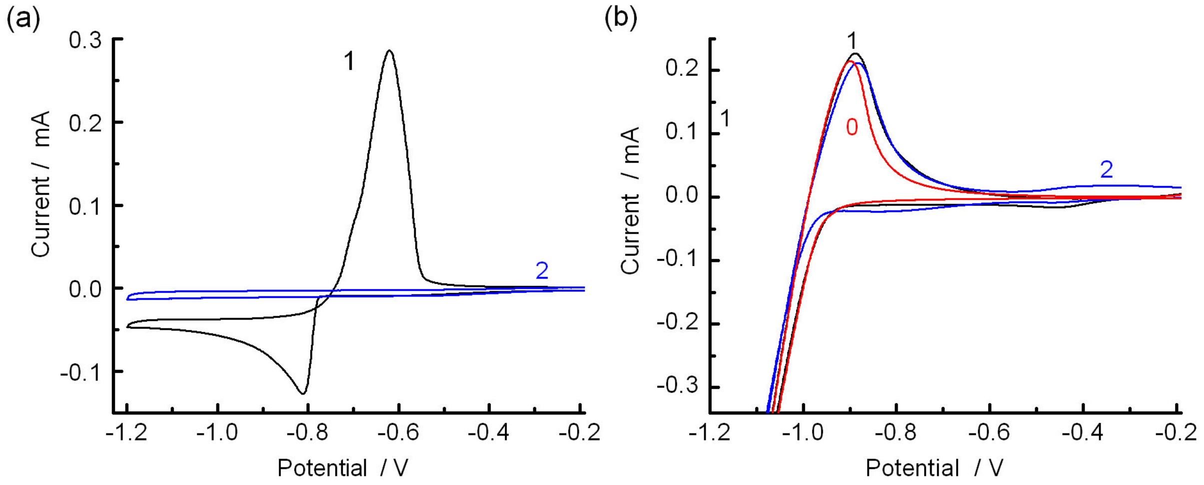

Fig. S1. Cyclic voltammograms of 2.0 mM $CdCl_2$ in 0.1 M KCl (pH 11) in (1) absence and (2) presence of 4.8 mM MAA on glassy carbon (a) and Te (b) electrodes. Scan rate: 50 mV s^{-1}. Curve 0 was obtained in the blank electrolyte.

Fig. S1b depicts the cyclic voltammogram of $CdCl_2$ 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 Te^{2-}, which has a formal potential of -1.16 V (*vs* Ag/AgCl).[S5]

$$Te^0 + 2e \longrightarrow Te^{2-} \qquad (5)$$

During the back sweep, a small anodic peak was observed due to the oxidation of Te^{2-} to Te at the potential of -0.89 V. It indicated that only a fraction of Te^{2-} 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.

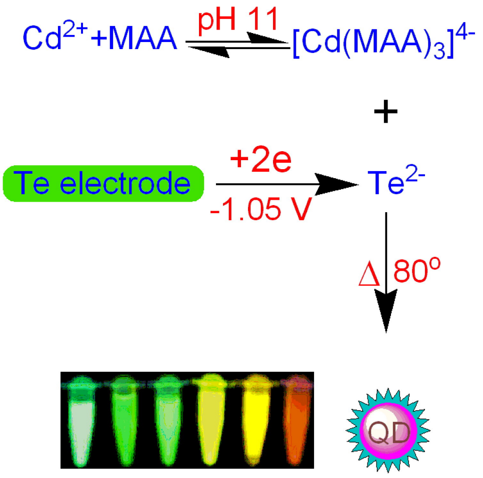

Fig. S2. Schematic depiction on one-pot synthesis of CdTe QDs with cathodic tellurium electrode in presence of MAA.

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.

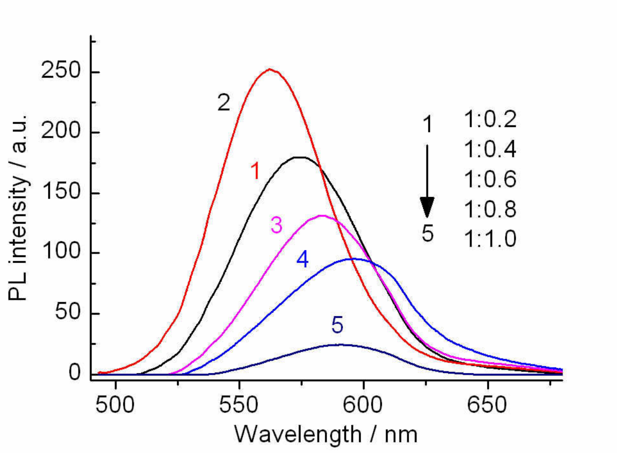

Fig. S3. PL spectra of MAA-capped CdTe QDs with different ratios of Cd to Te. The PL intensities are 179.8 (1:0.2), 252.4 (1:0.4), 131.6 (1:0.6), 95.2 (1:0.8) and 24.3 (1:1), respectively. Excitation wavelength: 388 nm.

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.

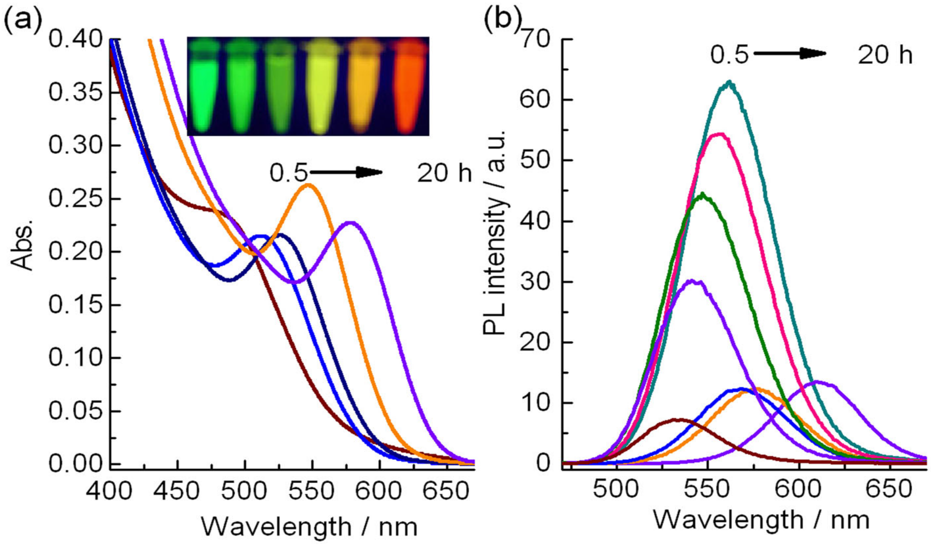

Fig. S4. UV-Vis absorption (a) and PL (b) spectra of ACYS-capped CdTe QDs obtained with different heating durations. The absorption peaks occur at 482, 499, 512, 525, 532, 540, 547 and 578 nm for 0.5, 2, 4, 8, 10, 12, 14 and 20 h, respectively, while the PL emission peaks occur at 532, 541, 547, 557,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

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 maxumum value of 79.0 % at 8 h. The further increaing heating duration resulted in the decrease of QY.

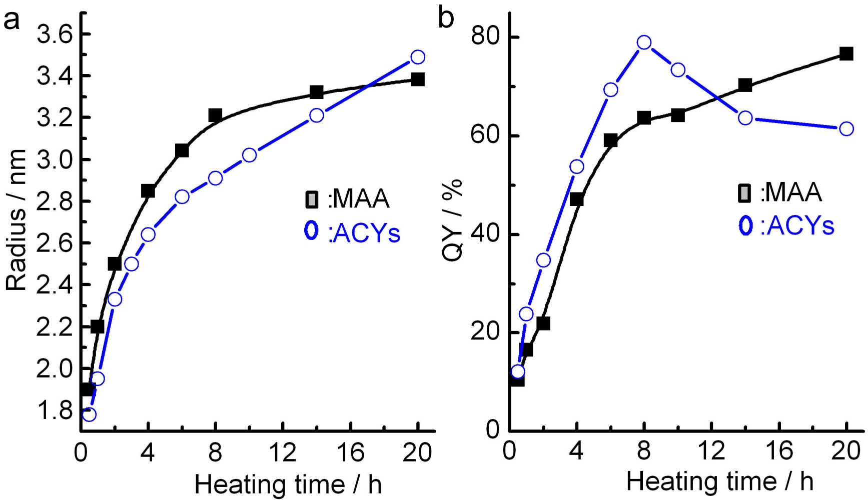

Fig. S5. Comparison of diameter (a) and quantum yield (b) evolution profiles for MAA-stabilized (■) and ACYS—stabilized(○) CdTe QDs with heating durations at 80 ^{0}C.

References

S1 J. N. Demas and G. A. Grosby, *J. Phys. Chem.*, 1971, **75**, 991.

S2 Y. Okinaka, by A. J. Bard, R. Parsons and J. Jordan, (Eds.) *Standard Potentials in Aqueous Solution,* New York, Marcel Dekker, 1985, pp. 257.

S3 A. Shavel, N. Gaponik and A. Eychmller, *J. Phys. Chem. B*, 2006, **110**, 19280.

S4 I. Turyan and D. Mandler, *Electrochim. Acta,* 1995, **40**, 1093.

S5 P. R. Panicker, M. Knaster and F. A. Kroger, *J. Electrochem. Soc.*, 1978, **125**, 566.