Synthesis of CdTe QDs by hydro-thermal method, with tunable emission fluorescence

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Supporting Information

Contents:

Determination of the concentration of Cd and Te in CdTe QDs

A new method, combining absorption spectrum and emission spectrum, was employed to achieve the accurate concentrations of Cd and Te in obtained CdTe QDs. Both Cd^{2+} and Te^{+4} can react with Rhodamine B (denoted as RhoB) into compounds $(RhoB)_4[TeI_8]$ and $(RhoB)_4[CdI_6]$ (denoted as Te-RhoB and Cd-RhoB), respectively, with absorption peak at 580nm but with different absorption factors [Rao 1983; Kim 2012; Talio 2012]. Therefore, an equation set was created by fitting the absorption intensity and emission intensity of Cd-RhoB/Te-RhoB solution, to determinate the concentrations for each component. The detailed process was as follows: Te standard solution, 1 mL of 1M H_2SO_4, 0.5 mL of 20% KI and 0.5 mL of 1% polyvinyl alcohol (PVA, Mw=50-85 k) were mixed and shaked up (this mixture is called as Solution 1), and then 0.5 mL of 0.05% rhodamine B was added slowly into Solution 1 and water was added until a constant volume of 10 mL. Five samples were prepared with final Te concentration of 0, 2, 4, 8 and 10×10^{-6}M. The formation of complex $(RhoB)_4[TeI_8]$ was solubilized by PVA. Cd standard solution was treated using the same procedure, with Cd concentrations of 0, 4, 8, 16 and 20×10^{-6}M. After storing in darkness for 30min, absorptions at 580nm of the samples were measured by UV-Vis, while a solution with the same concentrations of H_2SO_4, KI, PVA and RhoB was used as the background. The fitting of absorption data of Cd-complex and Te-complex are shown in Fig. S1. The intercepts for both fitted equations was fixed at 0.758 (the absorption of the mixture of H_2SO_4, KI, PVA and RhoB, without Cd or Te). The empirical fitting functions of the curves in Fig. S1 are provided as follows:

$$A_{Cd}=0.758+0.00968[Cd] \tag{1}$$

$$A_{Te}=0.758+0.01494[Te] \tag{2}$$

where A_{Cd} and A_{Te} are the absorption intensities of Cd-RhoB complex and Te-RhoB complex, respectively, while [Cd] and [Te] are the concentrations of Cd and Te expressed in micromolar. When combining the two equations Eq (1) and Eq (2), the absorption of a mixture of Cd and Te (A) is assumed to be Eq (3):

$$A=0.758+0.00968[Cd]+0.01494[Te] \tag{3}$$

Four samples mixing Cd and Te standard solutions, different [Te] and [Cd] were measured by UV-Vis to confirm Eq (3), and the results in Table S1 showed that the experimental results match the theoretical values calculated from Eq (3) with very tiny error, by which the assumed equation Eq (3) is proved to be accurate.
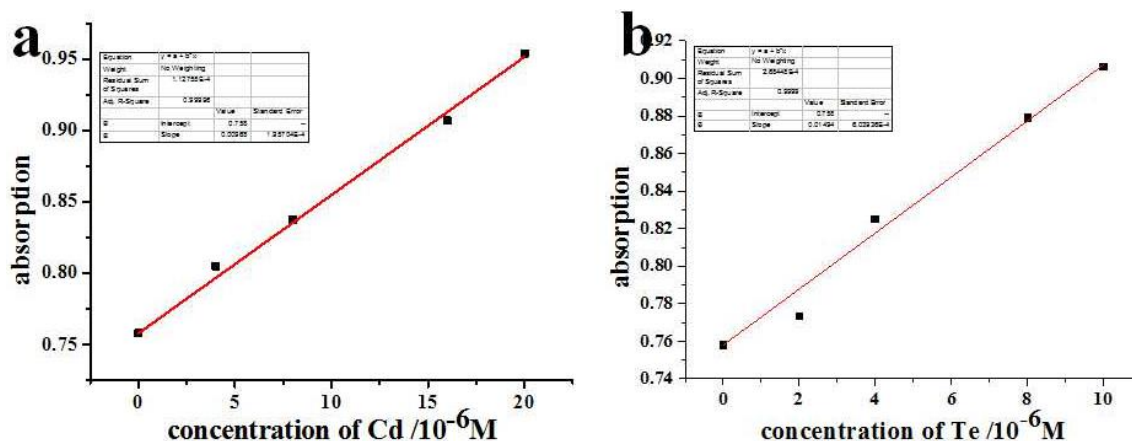
Fig. S1 Absorption intensity curves for Cd-RhoB complex and Te-RhoB complex.

Table S1 Verification of the assumed equation Eq (3), where A_{exp} and A_{cal} are the experimental absorption and the calculated result from Eq (3), respectively.

[Cd] /10^{-6}M	[Te] /10^{-6}M	A_{exp}	A_{cal}
5	5	0.88134	0.8811
5	10	0.96302	0.9558
10	5	0.93296	0.9295
10	10	1.00471	1.0042

To determine [Cd] and [Te], another equation is needed. Therefore, the fluorescence of above samples was measured to get corresponding Te and Cd standard fluorescence curves. The Cd-RhoB complex and Te-RhoB complex are non-fluorescent, so the decreased RhoB concentration, caused by the presence of Cd or Te, showed weaker fluorescence, compared to the un-treated rhodamine B. The parameters for measurements were excitation wavelength λ_{ex}=490nm, the excitation and emission widths s_{ex}=s_{em}=4nm. The data for Cd-complex and Te-complex are shown in Fig. S2-a and Fig. S2-b, respectively. The intercepts for both fitted equations was fixed at 162.323 (the fluorescence intensity of rhodamine solution without Cd or Te). The fitting equations for Cd-complex and Te-complex are as follows:

$$Int_{Cd}=162.323-4.18624[Cd] \qquad (4)$$

$$Int_{Te}=162.323-4.46689[Te] \qquad (5)$$

where Int_{Cd} and Int_{Te} are the fluorescence integral intensities of Cd-RhoB complex and Te-RhoB complex, respectively. So intensity for a mixture of Te-complex and Cd-complex is expected to be:

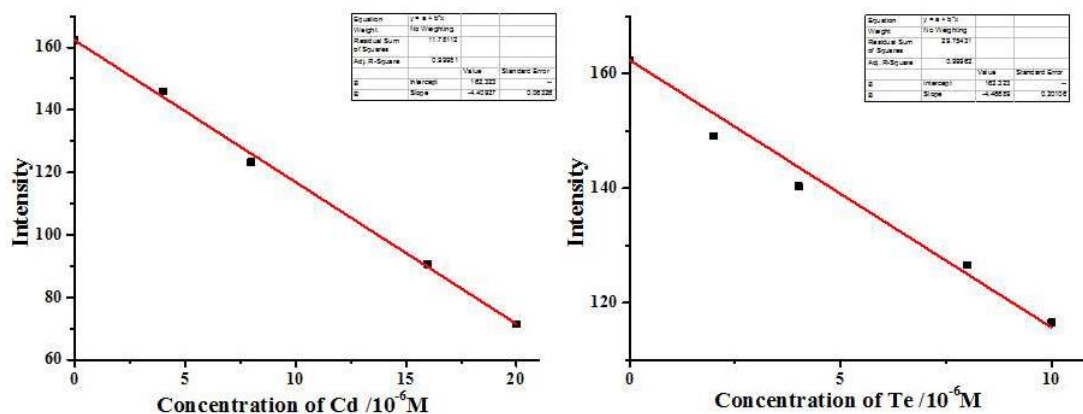$$Int=162.323-4.18624[Cd]-4.46689\ [Te] \tag{6}$$

Fig. S2 Emission intensity curves for Cd-RhoB complex and Te-RhoB complex.

By combining Eq. (3) and Eq. (6), an equation set was obtained to get the vales of [Cd] and [Te]:

$$\begin{cases} A=0.758+0.00968[Cd]+0.01494[Te] \\ Int=162.323-4.18624[Cd]-4.46689\ [Te] \end{cases}$$

To obtain the accurate values of [Cd] and [Te], 1mL CdTe QDs colloid sample was treated by dialysis for 24h, followed by adding 0.3mL H_2O_2 and 0.6mL HNO_3, which was subsequently treated by the microwave digestion. The obtained liquid was collected into a volumetric flask and distilled water added to make the total volume equal 10mL. 0.5mL of this solution was mixed with 1mL of 1M H_2SO_4, 0.5mL of 20% KI and 1mL 1% PVA (Mw=50-85kDa) and shaken up. Then 0.5mL of 0.05% RhoB was slowly added in, followed by diluted into 10mL. Both of absorption and emission spectra were done for this mixture, with the same parameters as for the standard solutions. Through the above equation set, the data and calculation results for 10 CdTe QDs samples with different synthesizing parameters are shown in Table S2.

Table S2 Calculations of [Cd] and [Te] in CdTe QDs samples, T is the reaction temperature, t is the heating time, $[Cd]_i$ and $[Te]_i$ are the initial concentrations of Cd and Te before the starting of reaction, respectively, $[Cd]_e$ and $[Te]_e$ are the concentrations of Cd and Te in the samples obtained after microwave treatment and reaction with rhodamine-B respectively, $[Cd]_s$ and $[Te]_s$ are the concentrations of Cd and Te in CdTe QDs colloid before the microwave digestion, respectively.

Sample	1	2	3	4	5	6	7	8	9	10
$T./^oC$	140	140	140	140	100	120	160	140	140	140
t /h	0.5	1	1.5	2	1	1	1	1	1	1
$[Cd]_i$/mM	5	5	5	5	5	5	5	2.5	7.5	10
$[Te]_i$/mM	1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25
A	0.995	0.968	1.044	0.990	0.989	0.983	1.019	0.927	1.010	1.014
Int	71.65	83.63	50.67	73.94	74.11	76.86	61.34	101.30	65.89	64.18
$[Cd]_e/10^{-6}M$	15.226	12.330	20.169	14.762	14.723	14.104	17.788	8.061	16.397	16.824
$[Te]_e/10^{-6}M$	6.028	6.061	6.094	5.952	5.950	5.916	5.937	6.107	6.222	6.204
$[Cd]_s$/mM	3.0453	2.4660	4.0338	2.9524	2.9446	2.8208	3.5575	1.6122	3.2795	3.3648
$[Te]_s$/mM	1.2056	1.2123	1.2188	1.1904	1.1900	1.1832	1.1874	1.2215	1.2444	1.2408

Determination of the quantum yield (QY) of the CdTe QDs

To get the QY of CdTe QDs, Rhodamine 6G was employed as the reference. Rhodamine 6G was dissolved in water with the same molar concentration as tellurium in CdTe QDs colloid, and placed in the 1-cm quartz cuvette. Fluorescence spectra were collected between 480 and 800 nm at room temperature. The QY of CdTe QDs is calculated with the following equation:

$$\Phi_x = \Phi_r \left(\frac{Int_x}{Int_r} \right) \left(\frac{n_x^2}{n_r^2} \right) \tag{7}$$

where *Int* is the integral intensity of fluorescence peak, and *n* is the refractive index of the solution. The *x* and *r* subscripts refer to the detected sample and the reference, respectively. The QY of the reference rhodamine 6G is fixed at Φ_r=95% [Murray 1993], and the results are shown in Table S3.

Table S3 Calculations of quantum yield for CdTe QDs samples, T is the reaction temperature, t is the heating time, $[Cd]_i$ and $[Te]_i$ are the initial concentrations of Cd and Te before the starting of reaction, respectively, $[Cd]_s$ and $[Te]_s$ are the concentrations of Cd and Te in detected CdTe QDs colloid samples, respectively. Int_{Rho6G} and Int_{CdTe} are the integral intensity of emissions for rhodamine 6G and CdTe QDs, respectively.

| Sample	1	2	3	4	5	6	7	8	9	10
T./^{o}C	140	140	140	140	100	120	160	140	140	140
t /h	0.5	1	1.5	2	1	1	1	1	1	1
$[Cd]_i$/mM	5	5	5	5	5	5	5	2.5	7.5	10
$[Te]_i$/mM	1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25
$[Cd]_s$/mM	3.0453	2.4660	4.0338	2.9524	2.9446	2.8208	3.5575	1.6122	3.2795	3.3648
$[Te]_s$/mM	1.2056	1.2123	1.2188	1.1904	1.1900	1.1832	1.1874	1.2215	1.2444	1.2408
Int_{Rho6G}	50315.9	50478.8	50787.8	49639.2	49513.9	49075.4	49488.9	50725.2	51936.4	51786.1
Int_{CdTe}	21018.8	25131.3	22913.0	26640.1	4796.1	12994.9	15594.3	1591.9	51003.3	51003.3
Φ_x	39.68	47.29	42.85	50.98	9.20	25.16	29.93	2.98	93.29	93.57
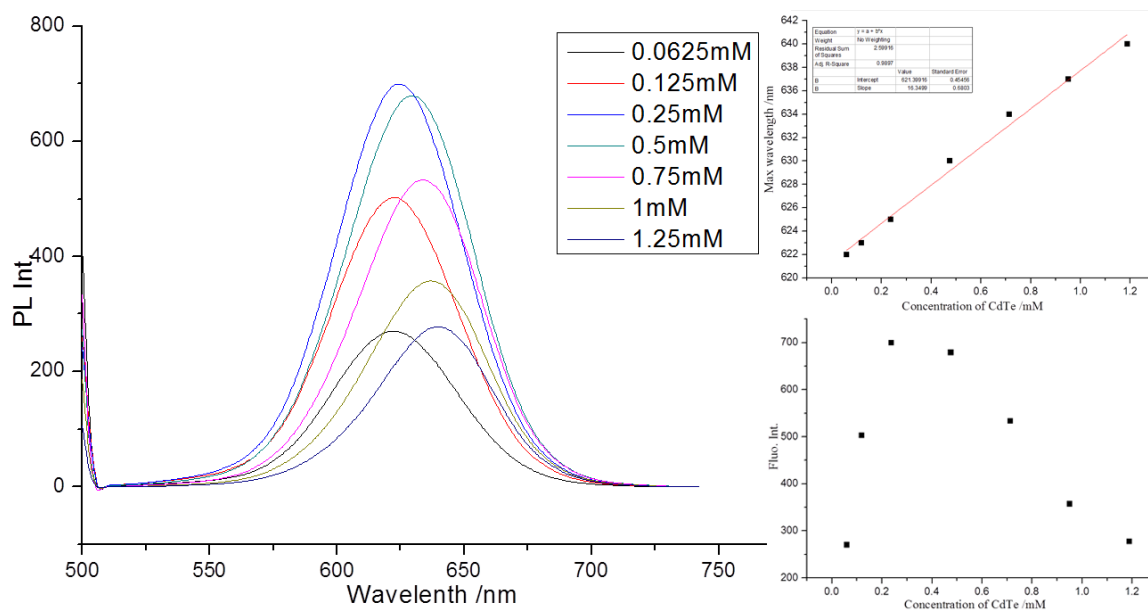
Fig. S3 *Emission spectra of CdTe QDs with different concentrations (λ*_{ex}*=500nm)*
Fitting of the wavelength for max fluorescence intensity as a function of the CdTe concentration and changes of fluorescence intensity with increasing the CdTe concentration.

Fig. S4 *Emission spectra of CdTe QDs with different concentrations (λ_{ex}=590nm)*
Fitting of the wavelength for max fluorescence intensity as a function of the CdTe concentration and changes of fluorescence intensity with increasing the CdTe concentration.
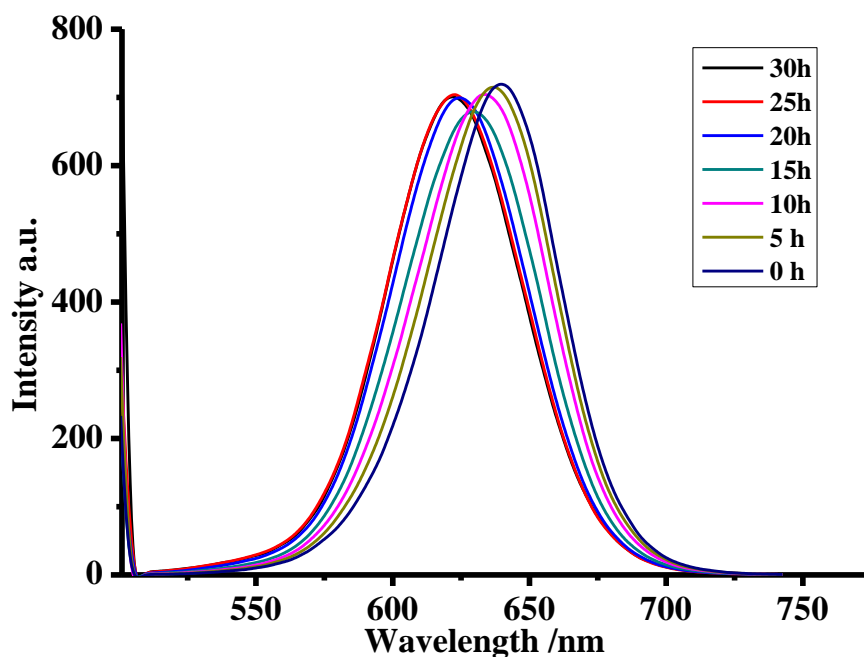

Fig. S5 TEM picture of CdTe QDs (The synthesis conditions sample were t=1h, T=160°C and Cd/Te=4/1).

Fig. S6 Photo-stability of as-prepared CdTe QDs (λ_{ex}=500 nm)

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