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MONITORING FLUORESCENCE LIFETIME CHANGES OF CdTe QDs SYNTHESIZED WITH DIFFERENT STABILIZERS BY PHOTOLUMINSCENCE AND ZETA POTENTIAL MEASUREMENT

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In today science, One of the capable uses of nanomaterials is bio-applications which make good use of the specific properties of nanoparticles such as semiconductor nanoparticles show strong emission of visible light for a long time. However, since the nanoparticles will be used both *in-vivo* and *in-vitro*, their stability is an important issue to the scientists concern. In this dissertation, we are going to test the stability of semiconductor quantum dots（CdTe） in a number of media including the bio-compatible medium and their behaviors will be illustrated in terms of optical properties change and aggregation degree.

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*Keyword:*Semiconductor quantum dots; Stability test; Bio-application; Aggregation

1. Introduction

CdTe nanocrystals capped by short-chain thiol molecules can easily be prepared in aqueous solution, possess a single narrow emission band and can potentially be used in biological research [1， 2]. Colloidal semiconductor nanocrystals (NCs) with size dependent optical properties and variable surface chemistry determined by capping ligands have extensively been used in the last several years as luminescent species for imaging, detection and biolabeling [3]. Semiconductor nanocrystals, which are also known as quantum dots (QDs), are single crystals with diameter of a few nanometers. [4-10] There are a few types of semiconductors can be used to make QDs, for example II-IV semiconductor such as cadmium selenide (CdSe) and III-V one such as indium phosphide (InP). By varying the composition and the size of semiconductor, QDs with different band gaps can be synthesized. Difference from bulk semiconductor, the size of QDs is comparable to or smaller than Bohr exciton radius [5]. The electron – hole pairs, which are known as excitons, generated by absorption of photons which have energy larger than the band gap of the QDs are confined into the small QDs, so they experience quantum confinement effect and hence their energy levels are discrete instead of a continuous energy band [4].

The size and shape band gap of QDs can be tuned by precise control of the synthetic process in terms of time, temperature and types of stabilizer and hence the band gap of QDs can be

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controlled. [4,7] Due to the feasibility of tuning the band gap, QDs made of the same composition can also give different emission spectrum, i.e. different colors.

Bio-applications of the nanoparticles are one of the areas scientists are working hard in order to understand the special properties of the nanoparticles. For example, semiconductor nanoparticles have strong luminescence in visible range over a long period of time; As they are used both *in-vitro* and *in-vivo*, it is important to ensure that they are stable in different media [11-15], which is also used for synthesis, properties and bio-application of CdTe QDs reported by others [16-26] .

The objectives of this dissertation are to check the stability semiconductor nanoparticles in different media, e.g. water and various buffers, in terms of:

1) the change in optical properties and;
2) the degree of aggregation

to identify their possible usage in bio-applications. Different surface coatings of nanoparticles will be used to test the stability of the nanoparticles in different surrounding media.

2. Experimental

2.1 Synthesis of TGA（Thioglycolic acid）-CdTe nanocrystals

First, 0.4mmol of $Cd(CH_3COO)_2 \cdot 2H_2O$, 0.08mmol of Na_2TeO_2 and 160mg of $NaBH_4$ were weighed. Second, the $Cd(CH_3COO)_2 \cdot 2H_2O$ was dissolved in 50mL Milli-Q water and then poured into a stand – up flask with a magnetic bar and the solution was kept stirring. Next, 100mL of Milli-Q water followed by 36μL of TGA was added into the flask. Then, the pH of the solution was adjusted to 11.5 with 1M NaOH solution and then the $Na_2TeO_3$was dissolved in 50mL Milli-Q water. After 5minutes, the $Na_2TeO_3$and then followed by the $NaBH_4$ were added to the solution and waited for another 5minutes. After that, the flask was connected to a condenser and undergone reflux at 100^{o}C under open-air conditions up to 7hours. Finally, the solution was poured into a bottle with filtration after cooling and stored at +4^{o}C without washing [27,28].

2.2 Synthesis of TG（1-thioglycerol）- and MA（Mercaptoamina）-CdTe nanocrystals

QDs are washed with isopropanol before use. We chose some buffers with different properties such as pH and composition to check the NPs stability as shown in Table. 1.

Table.1Buffers tested for NPs stability

	pH	pH variation	Composition	Manufacturer
1	4	±0.02	Potassium hydrogen phthalate	VWR international Ltd.
2	7	±0.02	Potassium dihydrogen phosphate/ disodium hydrogen phosphate	VWR international Ltd.
3	8	±0.02	Borate	VWR international Ltd.
4	10	±0.05	Borate	VWR international Ltd.
5*	/	/	Cell culture media	Sigma-Aldrich Co. LLC.

*Buffer number 5 we will call in text as bio-buffer.

In the experiment, we diluted the QDs in a plastic cuvette. Then, we checked both absorption and PL spectra of QDs and the absorption spectrum with time – scale from 0 minute up to a week after the NPs were added. The dilution of QDs in Milli-Q water and buffer number 1-4 are shown in Table.2.

Table.2Dilution of QDs in Milli-Q water and buffer number 1-4 andin Milli-Q water and buffer number 1-5

Name of NPs	Volume of NPs added (mL)	Volume of buffer/Milli-Q water added (mL)	Dilution (time)
TGA-CdTe(green)	0.2	2.8	15
TGA-CdTe(red)	0.2	2.8	15
MA-CdTe	1.5	1.5	2
TG-CdTe	0.2	2.8	15

For the bio-buffer, due to the presence of biomolecules and the color of it will absorb light, the PL of QDs will have a low intensity, so larger volume of QDs is needed to be added. The dilution of QDs in the bio-buffer is indicated in Table.3.

Table.3 Dilution of QDs in the bio-buffer

Name of NPs	Volume of NPs added (mL)	Volume of bio-buffer added (mL)	Dilution (time)
TGA-CdTe(green)	1.2	1.8	2.5
TGA-CdTe(red)	0.3	2.7	10
MA-CdTe	1.2	1.8	2.5
TG-CdTe	0.75	2.25	4

3. Results and discussion

3.1 CdTe synthesis

Following is the TGA-CdTe QDs we synthesized by one pot method [7].

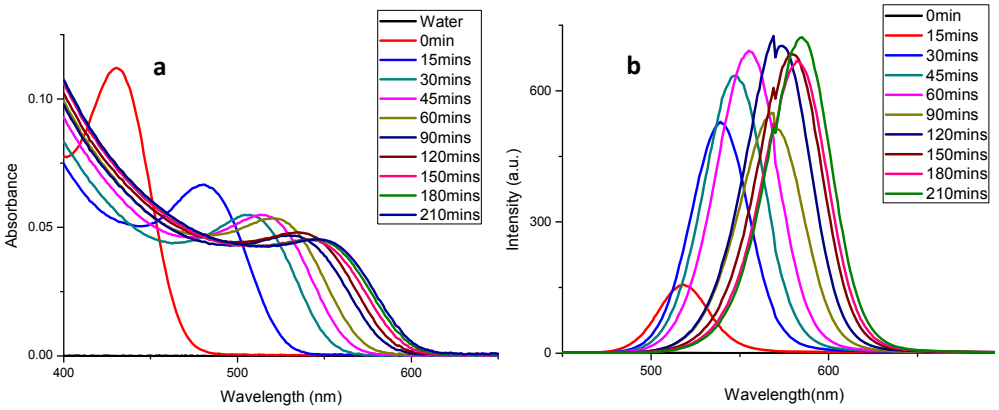

Fig.1a) Absorption and b) PL spectra of CdTe at different times during synthesis

Figure.1 shows the time dependent behavior of absorption and PL spectra during CdTe synthesis. Both of them show red shift with increasing synthesis time. This is because as time passes, the QDs grow larger and band gap decreases and hence causes the red shift of spectra. TGA-CdTe(green) and TGA-CdTe(red) were synthesized by a short time fluxing time and a long time fluxing time, respectively.

3.2 QDs stability

The stability of all kinds of QDs would be tested in different media.

3.2.1 Stability of TGA-CdTe(green) QDs in different media

For the first, we checked the stability of TGA-CdTe(green) QDs. Results of PL intensity and PL peak position of TGA-CdTe(green) QDs are shown in Figure.2 and Table.4 respectively.

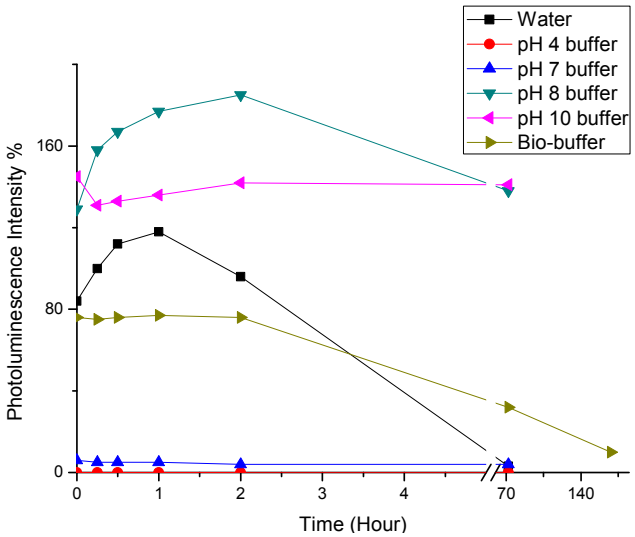

Fig..2Variation of PL intensity of TGA-CdTe(green) QDs in different media versus time

Table.4PL peak position variation of TGA-CdTe(green) QDs with time in different media

Time(hour)	0	0.25	0.5	1	2	72	168
Water	601	601	601	600	599	700	/
pH4 buffer	--	--	--	--	--	--	/
pH7 buffer	599	599	599	599	599	464	/
pH8 buffer	596	594	594	593	593	593	/
pH10 buffer	594	594	594	594	594	594	/
Bio-buffer	603	603	603	603	603	599	598

* "--" means no peak can be observed.
** "/" means no data is taken on that day.

TGA-CdTe(green) QDs in Milli-Q water

In the first 2hours, TGA-CdTe(green) QDs are fairly stable which only show a small blue shift in PL.But after 3days, a great decrease in intensity and red shift of peak in PL spectrum which represent that they are no longer stable. This may be due to the fact thatQDsare too diluted that the stabilizers loosen easily and hence causes the QDs to aggregate.

TGA-CdTe(green) QDs in pH4 buffer

TGA-CdTe(green) QDs in pH4 buffer are unstable in the buffer because no emission intensity and no peak of QDs can be detected by the PL spectroscopy at any time during the testing.

TGA-CdTe(green) QDs in pH7 buffer

TGA-CdTe(green) QDs in pH7 buffer show very low but steady emission intensity within the measurement period, which means that they are unstable in terms of loss in PL intensity. Stable peak position can be observed in the first 2hours and shows a blue shift after 3days. The blue shift may be due to degradation of QDs.

TGA-CdTe(green) QDs in pH8 buffer

The PL intensity of TGA-CdTe(green) QDs in pH8 buffer increases at the first 2hours and then shows a decreasing tendency after 3days. However, their peak position is very stable within the experimental time, which specifies that the TGA-CdTe(green) QDs concentration in pH8 buffer decreases but no degradation of QDs.

TGA-CdTe(green) QDs in pH10 buffer

TGA-CdTe(green) QDs'PL intensity in pH10 buffer varies less than 10% and their peak position is the same during the inspection time which indicate that they are very stable in the pH10 buffer.

TGA-CdTe(green) QDs in bio-buffer

TGA-CdTe(green) QDs in bio-buffer have stable PL intensity within the first 2hours and decreases moderately after 3days. Buttheir PL peak position is stable within the experiment time frame.

To sum up, TGA-CdTe(green) QDs in pH10 buffer have the best stability while those in pH4 buffer have the worst stability. Those for bio-applications should be used for less than one day.

3.2.2. Stability of TGA-CdTe(red) QDs in different media

TGA-CdTe(red) QDs have a larger size than TGA-CdTe(green) QDs but their stabilizer are the same. Results of PL intensity and PL peak position of TGA- CdTe(red) QDs are indicated in Figure.3 and Table.5 separately.

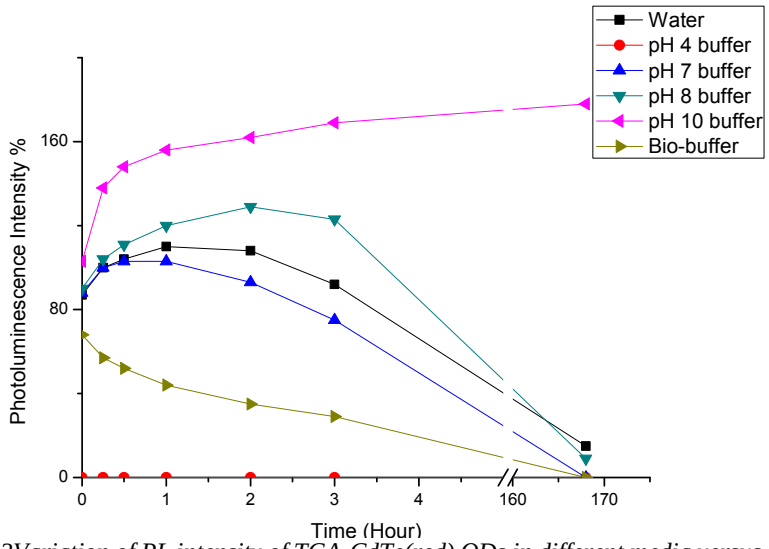

Fig.3Variation of PL intensity of TGA-CdTe(red) QDs in different media versus time

Table.5PL peak position variation of TGA-CdTe(red) QDs with time in different media

Time(hour)	0	0.25	0.5	1	2	3	168
Water	651	652	653	654	652	651	645
pH4 buffer	--	--	--	--	--	--	--
pH7 buffer	646	645	644	643	642	642	--
pH8 buffer	652	652	652	652	651	650	640
pH10 buffer	651	648	648	647	647	646	644
Bio-buffer	649	648	648	647	647	646	--

TGA-CdTe(red) QDs in Milli-Q water and pH7 buffer

The PL intensity of TGA-CdTe(red) QDs in Milli-Q water and pH7 buffer grow up in the first hour and then slowly goes down to 0% and 15% intensity respectively after 7days. But their PL peak positions in both Milli-Q water and pH7 buffer are stable. These mean that for TGA-CdTe(red) in both Milli-Q water and pH7 buffer is not stable for long time study.

TGA-CdTe(red) QDs in pH4 buffer

TGA-CdTe(red) QDs in pH4 buffer do not show any emission within the experimental duration, which means they are unstable in pH4 buffer.

TGA-CdTe(red) QDs in pH8 buffer

TGA-CdTe(red) QDs in pH8 buffer shows increase in PL intensity in the first 2hours and then the PL intensity drops slowly to about 10% at the 7days. And their PL peak position is very stable within the first 3hours but show a small blue shift in PL peak position after 7days. These mean TGA-CdTe(red) QDs in pH8 buffer are unstable for long time use.

TGA-CdTe(red) QDs in pH10 buffer

We can observe that the PL intensity of TGA-CdTe (red) QDs in pH10 buffer shows an increase trend to 160% in the first 3 hours and still can keep a high PL intensity thereafter. And their PL peak position is fairly the same in 7days. These indicate that TGA-CdTe(red) QDs are very stable in pH 10 buffer for long time study, e.g. 7days.

TGA-CdTe(red) QDs in bio-buffer

We can note that the intensity of emission of TGA-CdTe(red) QDs in bio-buffer is decreasing gradually within the 3hours and drops to zero after 7days. But their PL peak position is almost the same within the 3hours and they show no peak after 7days. These mean TGA-CdTe(red) QDs in bio-buffer is not stable.

In summary, TGA-CdTe(red) QDs in pH10 buffer are the most stable and those in pH4 buffer is the least stable. And they are not suitable for bio-applications. Compared with TGA-CdTe(green) QDs, both of them behave similarly in water, pH 4, pH 8 and pH 10 buffer but differently in pH7 and bio-buffer.

3.2.3. Stability of MA-CdTe QDs in different media

In comparison to the previous two TGA-CdTe QDs, they are negatively charged while MA-CdTe QDs are positively charged. Figure.4 and Table.6 show the PL intensity and PL peak position of MA- CdTe QDs correspondingly.

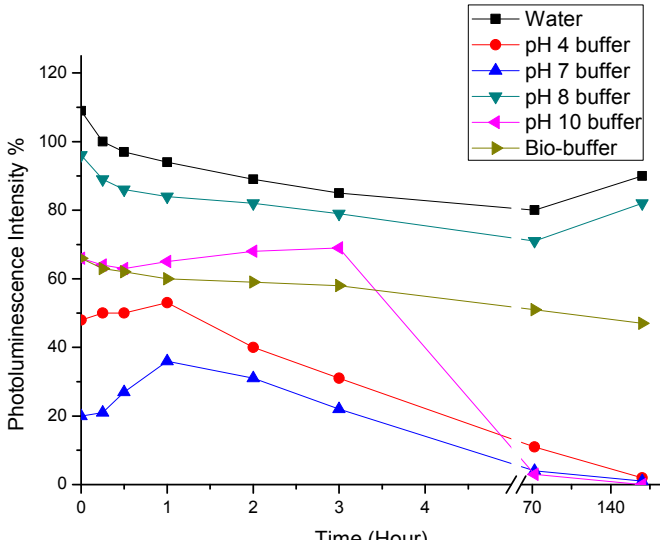

Fig.4Variation of PL intensity of MA-CdTe QDs in different media versus time

Table.6PL peak position variation of MA-CdTe QDs with time in different media

Time(hour)	0	0.25	0.5	1	2	3	72	168
Water	554	552	552	550	547	544	544	544
pH4 buffer	556	556	549	541	534	531	524	497
pH7 buffer	569	568	568	565	561	552	546	537
pH8 buffer	553	553	552	551	548	546	550	550
pH10 buffer	556	557	557	557	557	557	580	548
Bio-buffer	558	559	560	560	560	560	552	550

MA-CdTe QDs in Milli-Q water, pH8 buffer and bio-buffer

We can see that for MA-CdTe QDs in Milli-Q water, pH8 buffer and bio-buffer, they show little variation in PL intensity (within 20%) within 7days. However, the peak positions of MA-CdTe QDs in Milli-Q water and bio-buffer show a small blue shift which may be due to the QDs degrade while the peak position of MA-CdTe QDs in pH8 buffer has almost constant valve within the time of inspection. These mean that MA-CdTe QDs in both Milli-Q water, pH8 buffer and bio-buffer are quite stable but they are more stable in pH8 buffer because of nearly no peak shift of the PL intensity.

MA-CdTe QDs in pH4 buffer and pH7 buffer

MA-CdTe QDs in pH4 buffer and pH7 buffer demonstrategrowing PL intensity in the first hour and then constantly decrease to nearly 0% intensity after 7days and 3 days respectively. And both of them show a blue shift of peak position within the time of experiment which may be due to the degradation of QDs. These show that MA-CdTe QDs are unstable in pH4 buffer and pH7 buffer.

MA-CdTe QDs in pH10 buffer

MA-CdTe QDs in pH10 buffer illustrate an increase in PL intensity in the first 3hours and then drop rapidly to nearly 0% intensity after 3days.The peak position of PL intensity is very stable within the first 3hours but show peak shift afterwards. This represents MA-CdTe QDs is only stable for a short period but unstable for long time use.

In sum, MA-CdTe QDs are the most stable in pH8 buffer and are the least stable in pH7 buffer. In addition, they can be used for bio-applications. Compared with TGA-CdTe QDs, they have the best stability in pH10 buffer while MA-CdTe QDs have the best stability in pH8 buffer. This is because at a relative low pH buffer, i.e. pH8 buffer, NH_2 group of MA at the outer surface of MA-CdTe QDs will become NH_3^+ which provides them a very good electrostatic stabilization and at a relative high pH buffer, i.e. pH10 buffer, COOH group of TGA at the outer surface of TGA-CdTe QDs will convert to COO^- which also gives them a very good electrostatic stabilization. In pH4 buffer, TGA-CdTe QDs are dead as the pH value is too low that no COO^- can be formed; but MA-CdTe QDs still have PL at pH4 buffer since NH_3^+ can also be formed at low pH value .

3.2.4. Stability of TG-CdTe QDs in different media

Similar to TGA-CdTe QDs, TG-CdTe QDs are also negatively charged. But the difference is that TG is a bigger molecule (3 carbon length) containing 2 OH groups while TGA is a smaller molecule (2 carbon length) with 1 COOH group. Figure.5 and Table.7 show the PL intensity and PL peak position of TG-CdTe QDs individually.

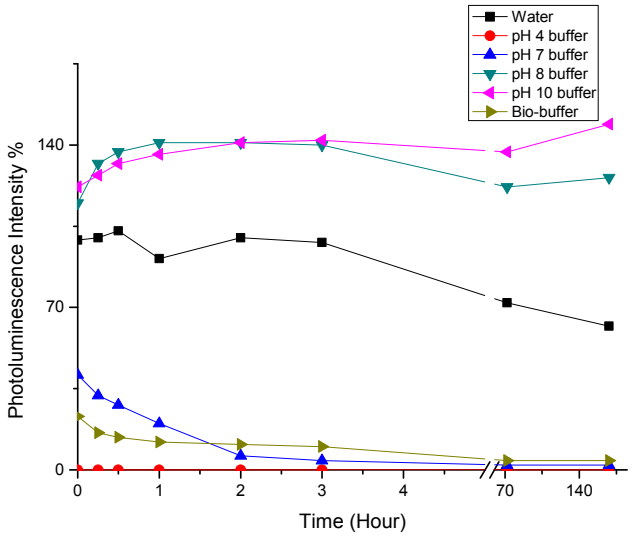

Fig.5Variation of PL intensity of TG-CdTe QDs in different media versus time

Table.7 PL peak position variation of TG-CdTe QDs with time in different media

Time(hour)	0	0.25	0.5	1	2	3	72	168
Water	554	552	552	550	547	544	544	544
pH4 buffer	--	--	--	--	--	--	--	--
pH7 buffer	588	587	586	586	584	587	568	567
pH8 buffer	594	591	589	589	588	588	586	585
pH10 buffer	599	598	597	596	595	595	590	590
Bio-buffer	592	592	591	591	589	589	585	583

TG-CdTe QDs in Milli-Q water

The PL intensity of TG-CdTe QDs in Milli-Q water is fairly stable within the first 3hours but showing a slow dropping tendencythereafter. And their PL peak positionhas a small blue shift up to 3hours and becomes stable after that. As TG-CdTe QDs in Milli-Q water still have a high PL intensity (about 70%) after 7days, so that they are quite stable in Milli-Q water.

TG-CdTe QDs in pH4 buffer

TG-CdTe QDs in pH4 buffer are unstable in the buffer since no emission intensity and no peak of QDs can be found by the PL spectroscopy at any time within the inspection time.

TG-CdTe QDs in pH7 buffer

TG-CdTe QDs in pH7 buffer have a rapid drop in PL intensity in the first 2hours from 40% to 6% and the PL intensity shows further decreasing subsequently. And their PL peak position shows a small blue shift. These indicate that TG-CdTe QDs is not stable in pH7 buffer.

TG-CdTe QDs in pH8 and pH10 buffer

The PL intensities of TG-CdTe QDs in both pH8 and pH10 buffer increase in the first 2hours and vary in about 10% within the experimental time. Moreover,their PL peak positions show a small blue shift in the inspection time. These mean TG-CdTe QDs in both pH8 and pH10 buffer are stable for long term study. And TG-CdTe QDs in pH10 buffer is more stable than in pH8 buffer as they did not show a drop of PL intensity in pH10 buffer.

TG-CdTe QDs in bio-buffer

ThePL intensity of TG-CdTe QDs in bio-buffer drops slowly within the inspection period but they have very low PL intensity (about 10 to 15%). And their PL intensity peak shows a small blue shift. These mean TG-CdTe QDs in bio-buffer is not stable.

To sum up, TG-CdTe QDs in pH10 buffer have the best stability and have the worst stability in the pH4 buffer. Moreover, they are not suitable for bio-applications. Compared to TGA-CdTe QDs, both of them are the most stable in pH10 buffer and the least stable in pH4 buffer. But TG-CdTe QDs are more stable than TGA-CdTe QDs in Milli-Q water and pH8 buffer. Furthermore, TG-CdTe QDs are much less stable than TGA-CdTe QDs in pH7 and bio-buffer.

3.3 Zeta potential and size

3.3.1 Zeta potential and size of TG-CdTe

For better understanding of the NPs, we need to check their charge and aggregation behaviors by the zetapotantial.

From Table.8, we can observe that during the first 3hours in water, the zeta potential of TG-CdTe QDs is slowly decreasing and their size remains approximately the same, about 30 to 50nm.This may be due to the formation of small clusters after washing. Later on, we can see that the cluster is growing up from 1 to 7days and the zeta potential nearly drops to zero after 3days which means the TG-CdTeQDs lose their stability.

Table.8Zeta potential and size of TG-CdTeQDs in Milli-Q water

Tme(hour)	Zeta Potential(mV)	Size (nm)
0	-27.4	58.8
1	-19.4	68.1
2	-20.8	32.7
3	-18.8	50.8
24	-14.2	1718.0
72	-0.6	1718.0
168	-2.45	396.1

However, the TG-CdTeQDs still have emission after 7days, as indicated in Figure.5, this shows that they lost colloidal stability but its PL stability is still reliable, i.e. theyare aggregated but still luminescent.

According to Table.9, in pH4 buffer, zeta potential of TG-CdTe QD is almost the same for all time ranges which is twice as low as their initial value in water. In addition, from 0hour to 3hours, we can notice that the aggregate size is more than 20times when compared with the TG-CdTe in Milli-Q water. Their PL intensity is same low at all the time, this means it is completely aggregated and surface traps were created which prohibit illumination.

Table.9Zeta potential and size of TG-CdTe QDs in pH4 buffer

Time(Hour)	Zeta Potential(mV)	Size (nm)
0	-14.6	1106.0
1	-18.3	2305.0
2	-19.1	1990.0
4	-20.1	1281.0
24	-19.3	1718.0
72	-13.2	955.4
168	-12.4	1990.0

In Table.10, the zeta potential of TG-CdTeQDs in pH10 buffer is very stable and its value is very similar to those of them at 0minute in Milli-Q water. Moreover, their size is also stable; it is a good agreement with PL behavior. This is the best data for stability where zeta potential and size is very stable all the time.

Table.10Zeta potential and size of TG-CdTeQDs in pH10 Buffer

Time(hour)	Zeta Potential(mV)	Size (nm)
0	-26.2	68.1
1	-26.8	43.8
2	-26.9	43.8
4	-29.4	21.0
24	-34.6	37.8
72	-24.0	53.8
168	-26.7	24.4

As shown in Table.11, compared with the TG-CdTeQDs in Milli-Q water, their zeta potential in bio-buffer is about 3 times drop but fairly stable.

Table.11 Zeta potential and size of TG-CdTeQDs in bio-buffer

Time(hour)	Zeta Potential	Size 1(nm)	Size 2(nm)	Size 3(nm)
0	-8.7	7.5	43.8	712.4
1	-10.7	7.5	43.8	825.0
3	-10.3	7.5	43.8	712.4
24	-10.2	7.5	43.8	531.2
72	-9.5	7.5	43.8	1106.0
168	-10.2	6.5	32.7	5560.0

For the case of size of TG-CdTe QDs is more complicated due to the presence of bio-molecules. We have 3 peaks, for the first two peaks, we can also observe in the pure bio-buffer, so these peaks are due to the bio-molecules. The third peak is the peak for TG-CdTe QDs, we can note aggregation occurs and the aggregates' size increases with time. This may be due to the adsorption of bio-molecules on the TG-CdTe QDs. However, they still has emission after 7days, it

may have a chance that either they only lose its colloidal stability but still has PL stability or the peak for the size of TG-CdTeQDs is hidden in the peak of the bio-molecules.

In sum, zeta potentials of TG-CdTe QDs in pH4, pH10 and bio-buffer are quite stable where that in Milli-Q water shows a decreasing trend. And TG-CdTe QDs in Milli-Q water, pH4 buffer and bio-buffer have aggregation while their size in pH10 buffer is very stable.

4. Conclusion

We have studied the behaviors of different QDs in different media for the aim of identifying the possible use of them for different pH media and finally for bio-applications.

From the results of CdTe QDs, in Milli-Q water, TGA-CdTe QDs show decrease while for MA- and TG-CdTe QDs is fairly stable in PL intensity after 7 days, but for TG-CdTe QDs, they show aggregation. In pH4 buffer, the PL intensity of negative charged TGA- and TG-CdTe QDs quenched followed with aggregation whereas positively charged MA-CdTe QDs still luminesce. In pH7 buffer, all of the QDs are not stable. In the pH8 buffer, TGA-CdTe QDs are unstable but MA- and TG-CdTe QDs are very stable. In pH10 buffer, positively charged MA-CdTe QDs are unstable while the negatively charged CdTe QDs are very stable. In bio-buffer, only positively charged MA-CdTe QDs are fairly stable which means that only MA-CdTe QDs is possible for bio-applications among the QDs we have studied.

To conclude, we found important information for the practical use of nanoparticles in bio-applications. MA-CdTe QDs is the best QDs for biological uses among the QDs. The analysis capability makes it the most suitable for key applications in (bio)system.

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