J Fluoresc (2012) 22:193–199
DOI 10.1007/s10895-011-0946-8

ORIGINAL PAPER

Microwave-Assisted Aqueous Synthesis of Highly Luminescent Carboxymethyl Chitosan-Coated CdTe/CdS Quantum Dots as Fluorescent Probe for Live Cell Imaging

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Received: 30 March 2011 / Accepted: 2 August 2011 / Published online: 20 August 2011
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Abstract This paper describes the development of a simplified and rapid method for the aqueous synthesis of quantum dots (QDs) with CdTe cores and gradient CdS external shells (CdTe/CdS QDs) aided by microwave irradiation. Several synthesis parameters, such as molar ratio of reagents, pH, reaction temperature, and reaction time, were studied in details. Under the optimized conditions, highly effective CdTe/CdS QDs could be synthesized in aqueous phase in only 15 min. In order to improve the biocompatibility of the CdTe/CdS QDs, these QDs were then interacted with carboxymethyl chitosan (CMC) so as they could be used as fluorescent probes in the aqueous phase. With the incorporation of CMC, the stability of modified QDs was found to have improved significantly (from 4 months to more than 10 months at room temperature). The photoluminescence quantum yield (PLQY) of the modified QDs could reach 75%, other parameters include a full width at half maximum of the emission (FWHM) spectrum as 40~60 nm, and an average size, estimated from electron microscopic images, as 3.5 nm. As fluorescent probes, these modified QDs were successfully used for imaging live Madin–Darby canine kidney (MDCK) cells, in which the preliminary results indicated that these modified QDs demonstrated good biocompatibility and showed promising applications for bio-labeling and imaging.

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Keywords Quantum dots · Aqueous synthesis · Carboxymethyl chitosan · Biological fluorescent labeling

Introduction

High-quality colloidal semiconductor nanocrystals (also referred to as quantum dots, QDs) have drawn significant attention due to their size-dependent properties and flexible processing chemistry over the past decade. A large number of high-quality QDs, such as CdSe, CdTe, and some alloy nanocrystals, were successfully synthesized by organometallic approach and the aqueous approach, respectively, with emission wavelengths ranging from visible to near-infrared. Several QDs were prepared in these ways, including CdS [1], CdSe [2] and CdTe [3, 4]. Compared to many organic solvents to be used as reaction media, water is inexpensive, nontoxic, nonflammable, and readily available. Considerable amount of research has been conducted on the use of water as a solvent for QDs synthesis [4–6]. Furthermore, the products from aqueous synthesis afford excellent water-solubility, stability, and biological compatibility [6]. However, QDs prepared in aqueous phase in general possess low quantum yields and broad full width at half maximum (FWHM) [7, 8] in emission spectrum. Additionally, the procedures in aqueous phase require very long reaction time ranging from several hours to several days [6]. In order to overcome these shortcomings in aqueous synthesis of QDs, some studies have utilized microwave irradiation in aqueous synthesis of QDs and have found that it provided a faster, simpler, and more energy efficient procedure compared to conventional hydrothermal synthesis [9–11]. Microwaves are electromagnetic waves and thus contain electric and magnetic fields, which produce a force on charged particles and cause them to move (or rotate) or to

further polarize [12]. The rapid change of the force direction creates friction and collisions of the molecules. Water molecule is a good media for microwave heating, because of its large dipole moment. Comparing to conventional hydrothermal synthesis techniques, synthesis of QDs by microwave irradiation was generally faster, simpler, and much more energy efficient [13–15].

At the present, the most promising application of QDs is their usage as fluorescent markers in the field of biology and medicine [16–19], hence the safety of their use is an important issue. The potential toxicity of QDs' has been subjected to close scrutiny. Most studies suggested that the physicochemical properties of surface coatings applied to the QDs were the dominant factors to affect QDs toxicity [20, 21]. In order to reduce QDs' cytotoxicity, surface modification is very important.

Chitosan is a cationic biopolymer prepared from alkaline N-deacetylation of natural chitin. Chitosan has been considered as a biodegradable, non-toxic, biocompatible, and environmental friendly material with many superior properties [22–25]. However, the poor solubility of Chitosan in water or common organic solvents limits its application. Carboxymethylation is an efficient means to convert chitosan into a water-soluble material. Carboxymethyl chitosan (CMC) has many unique chemical, physical, and biological properties such as low toxicity, excellent biocompatibility, and good ability to form films, fibers, and hydrogels [26]. It is an ideal material for QDs' surface modification.

In this paper, we describe a method that we have developed, in which alloyed QDs with CdTe cores and gradient CdS external shells are synthesized in aqueous phase with microwave irradiation under controlled temperatures in 15 min. Fluorescence probes with different colors were assembled by mixing CMC with CdTe/CdS core/shell quantum dots in the aqueous phase to form CMC-coated CdTe/CdS QDs (CMC-QDs). The colors of the probes as the final products depend upon the size of the original CdTe/CdS QDs. The fluorescent probes thus prepared have good optical properties, with photoluminescence quantum yields (PLQY) up to 75%. The FWHM of the emission spectrum was about 40~60 nm. The fluorescent probe with good dispersibility can remain stable for more than 10 months at room temperature. To test the suitability of this product as fluorescent probes for live cell imaging, we used them to incubate MDCK cells and analyzed the images to assess their optical properties demonstrated in this application.

Materials and Methods

Synthesis of CdTe/CdS QDs by Microwave Irradiation CdTe precursors were prepared by way of the reaction between Cd^{2+} and potassium hydride tellurium (KHTe) solution following the previously reported procedure [27]. KHTe solution was produced by reacting potassium borohydride (KBH_4) with tellurium powder at 0 °C or below. Then, 0.15 mmol Thioglycolic Acid (TGA) was injected into nitrogen-saturated 1.25 mM $CdCl_2$ aqueous solution (100 ml), as a stabilizer. The pH value of the CdTe precursors with a concentration of 1.25 mM (referring to Cd^{2+} from here on) was adjusted to 11.4 using 1 M KOH. At this point no fluorescence was observed when the precursors were excited by UV light. Finally, the resulting CdTe precursors were transferred to a Teflon inner vessel placed inside a Milestone microwave digestion/extraction system, and heated by microwave irradiation. With irradiation of microwave, TGA gradually released sulfide ions in aqueous solution, which in turn resulted in the formation of an alloyed structure.

Preparation of CMC-QDs Fluorescent Probe Different amounts of the CMC solution (5 g/L) and the CdTe/CdS QDs solution (1.25 mM) were mixed and constantly stirred for 30 min at room temperature. CMC-QDs fluorescent probes were generated by chelation between amido and carboxyl groups in CMC with QDs.

MDCK Cells Labeling with CMC-QDs MDCK cells were plated in a 35 mm glass-bottomed Petri dish at a density of 5×10^4 cells/dish and grown in Dulbecco's Modified Eagle's Medium (DMEM) overnight at 37 °C in 5% humidified CO_2. The cells were labeled with 0.2 ml of CMC-QDs solution (1 mM) and 1.8 ml DMEM (final CMC-QDs' concentration 0.1 mM) at 37 °C in 5% CO_2 for 24 h and then rinsed with PBS twice before being imaged with a fluorescence microscope(Nikon 80i, Japan). Then the cells were trypsinized and suspended in PBS and analyzed with a flow cytometer(Becton, Dickinson and Company, USA).

Results and Discussion

The molar ratio of precursor solution was a key factor in the synthesis of QDs. To get an optimal molar ratio of Cd^{2+}: TGA: KHTe, we investigated fluorescence intensities of various molar ratios with the same heating time. To find the optimal portion for KHTe, different molalities of KHTe were tested for four selected Cd^{2+}/TGA ratios. The reaction temperature was 100 °C. As shown in Fig. 1, the optimal molar ratio of Cd^{2+}: TGA: KHTe, which yielded the strongest fluorescence intensity of QDs, was 2.5:3:1. From here on, we fixed this as the optimal molar ratio of Cd^{2+}: TGA: KHTe.

Dissociation of H^+ in TGA and stability of CdTe surface complexes were directly related to precursor's pH value.

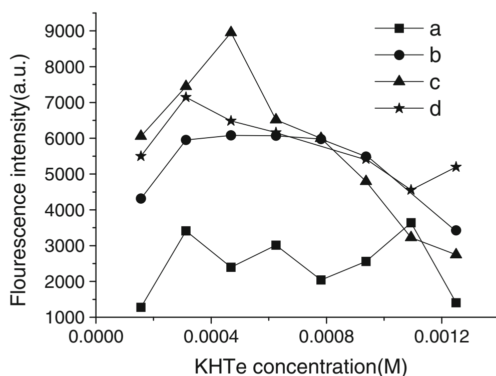

Fig. 1 Effect of precursor's molar ratios on CdTe/CdS QDs fluorescence intensity. Cd^{2+}:TGA=0.00125 M:0.001 M=2.5:2(**a**); Cd^{2+}:TGA=0.00125 M:0.00125 M=1:1(**b**); Cd^{2+}:TGA=0.00125 M:0.0015 M=2.5:3(**c**); Cd^{2+}:TGA=0.00125 M:0.00175 M=2.5:3.5(**d**)

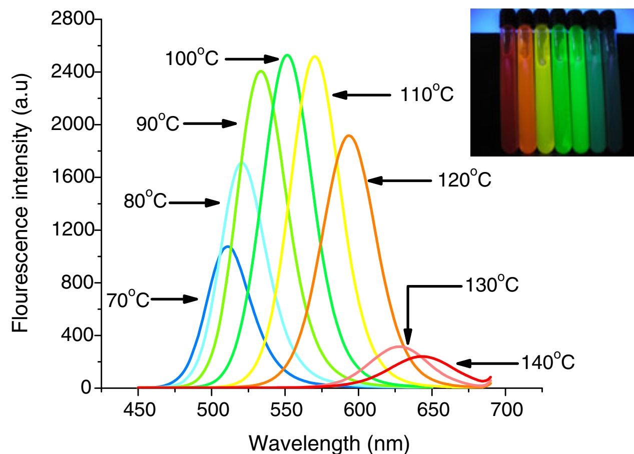

Fig. 3 QDs fluorescence spectra under different microwave irradiation temperatures. Insert is the image of corresponding QDs observed under ultraviolet light

TGA served as a stabilizer in the synthesis of QDs. At near neutral pHs, the solubility of TGA was very low. Obviously it could not work as a stabilizer ligand when insoluble. In our microwave synthesis, the favorable pH value of precursor solutions was found to range between 11.0 and 11.6, which was in keeping with those found in the conventional aqueous method [4]. Figure 2 demonstrates that the TGA-stabilized QDs showed pH-dependent photoluminescence, which is consistent with the previous reports [3, 4]. Specifically, the fluorescence intensity was gradually enhanced when pH of precursor solutions elevated from 9.5 to 11.0 and peaked between 11.0 and 11.6. Further increments of the pH led to a decrease in the luminescence of QDs. The reason for this behavior could be that along with increasing pH, more -SR ions were released from TGA molecules. An excessive number of stabilizer molecules might distort the surface, and consequently, the rough surface might give rise to new non-radiative defects [28].

Figure 3 shows that the reaction temperature plays an important role in determining the photoluminescence properties of CdTe QDs thus generated. With the microwave heating time set at 15 min, the colors of QDs gradually changed from blue to red along with the increasing temperature. This indicated that the size of the quantum dots gradually increased. But meanwhile the fluorescence intensity of the quantum dots underwent a course of gradual increasing to a rapid diminishing. It has

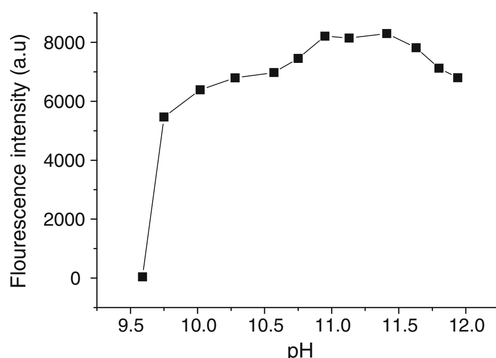

Fig. 2 Fluorescence intensity of as-prepared CdTe/CdS QDs versus different pH values of initial precursor solutions

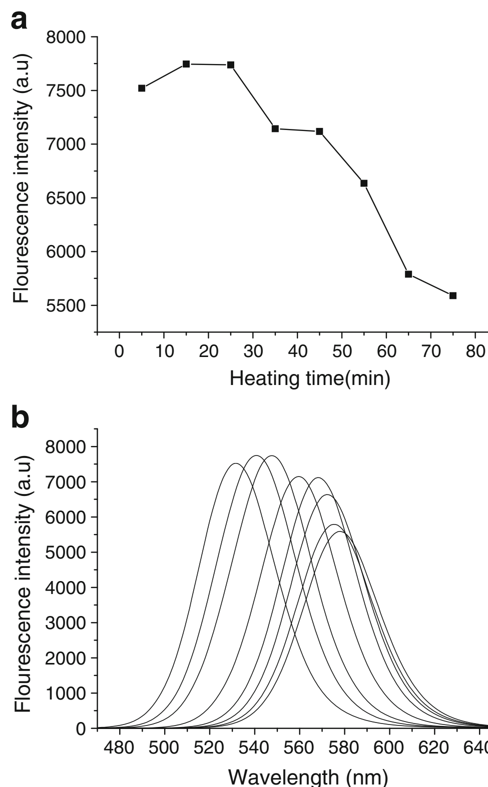

Fig. 4 **a** Temporal fluorescence intensity of QDs during their growth at 100 °C. For all samples [Cd^{2+}]: [TGA]: [KHTe]=2.5: 3: 1, [Cd^{2+}]= 1.25 mM, and pH=11.4. **b** Corresponding fluorescence spectra at different heating time. From left to right, heating time is 5, 15, 25, 35, 45, 55, 65, 75 min

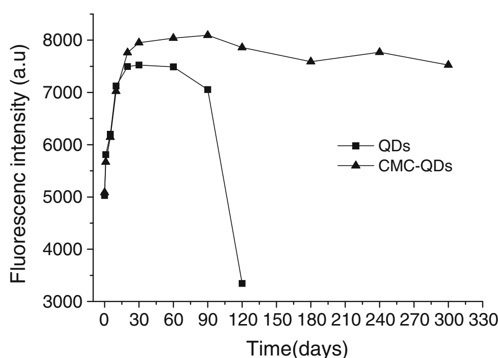

Fig. 5 Fluorescence intensity evolution of QDs and CMC-QDs at room tempurature

been demonstrated in previous work that temperature has a significant influence on the attaching/detaching rate of ligands from the QDs surface [29, 30]. When the temperature exceeded 110 °C, the equilibrium of the attaching/detaching of the monomer was destroyed. Excessive temperatures caused detachment of the ligands from the surface of the QDs and an increase in rate of complex formation, which resulted in a large amount of surface defects and thus a significant decline of fluorescence intensity. In addition, within a colloidal solution, the structure of colloidal nanocrystals would be destroyed when the irradiation temperature was too high. Precipitation would be formed and the fluorescence intensity would be adversely reduced.

As already known, the size of QDs is temperature dependent under fixed pH values and fixed ratio(s) of ligand and monome. Figure 4a shows the fluorescence intensity of QDs at different heating time. Varying the heating time at the optimal temperature(100 °C) can lead to production of different sizes of CdTe/CdS QDs. The evolutional emission peak position of CdTe/CdS QDs synthesized at 100 °C is shown in Fig. 4b. As clearly displayed in the graph (Figs. 4a and b), the fluorescence intensity of QDs declined when heating times extended beyond 25 min. The emission peak moved to longer

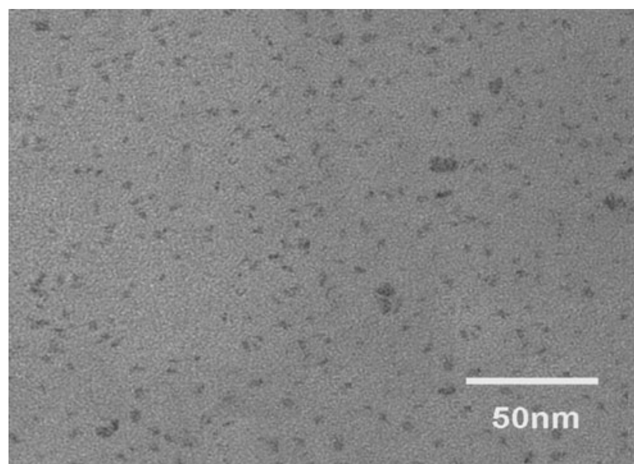

Fig. 7 Electron microscope image of CMC-QDs

wavelength as the heating time prolonged. The maximum emission wavelength shifted from 531 nm to 578 nm, and the emission color of QDs changed from green to yellow.

It is commonly known that the QDs with the same size and same photoluminescent properties display the same emission wavelengths. Therefore, by comparing the fluorescence spectra of QDs synthesized by changing the reaction temperature and the heating time, we can conclude that a more efficient way to get larger QDs with the optimal fluorescence intensity will be by way of changing the reaction temperature, rather than prolonging the heating time. The optimum temperature and heating time observed in our investigations were 100 °C, 15 min, respectively. Under this set of conditions, the fluorescence intensity of CdTe QDs was found to be the strongest.

The QD and CMC-QD solutions of the same molar concentration(1 mM) were placed in reagent bottles and stored at room temperature. The fluorescence intensities of both solutions were measured periodically and plotted again the time spans. Figure 5 shows the evolution of fluorescence intensity of QDs and CMC-QDs solutions illuminated by ambient light at room temperature. The

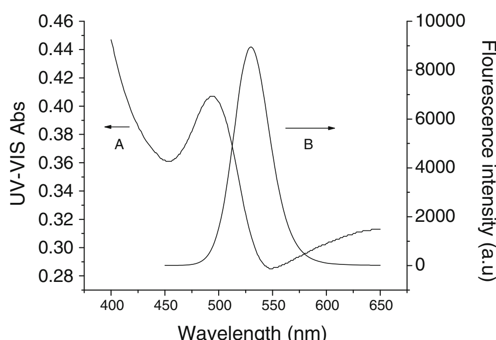

Fig. 6 UV–VIS absorption spectra (**a**) and photoluminescence spectra (**b**) of CMC-QDs fluorescent probe

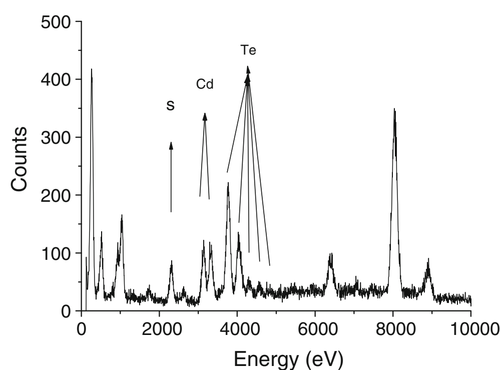

Fig. 8 EPMA X-Ray spectrum of CMC-QDs

Table 1 Relationship between the average cell fluorescence intensity and concentration of fluorescent probe

concentration of CMC-QDs(mM)	0	0.025	0.05	0.10	0.25	0.5
Average fluorescent intensity (a.u.)	45.38	50.07	53.94	284.37	3468.63	5132.98

fluorescence intensities of both QDs increased by about 60% in the first 10 days, and remained stable throughout approximately 30 days. This is in agreement with published results that the illumination method played an essential role both in enhancing the luminescent property and in improving PLQY of QDs [31–33]. According to earlier reports, the photoluminescence efficiency of QDs increased at the initial stages of photooxidation, due to the etching of tellurium trap states and an improvement of the CdS shell [4]. Precipitation began to appear in QDs solution and the fluorescence decayed away after 4 months. It could be due to photocatalytic oxidation of thiol molecules on the surface of CdTe/CdS QDs, as reported elsewhere for thiol-capped CdSe nanocrystals [34]. The thiol ligands on the surface of the QDs converted into disulfides under irradiation, leading to precipitation of the QDs because of depletion of the thiol source. However,CMC-QDs solution's fluorescence intensity remained largely unchanged and no coagulation was observed after 10 months. A possible reason for this could be that CMC, as a surface coating material, provided protection to maintain the structure of QDs after incorporating into quantum dots. This may be responsible for our observation that the stability of CMC-QDs was better than that of QDs.

Figure 6 displays the UV–VIS absorption spectra (A) and photoluminescence spectra (B) of the fluorescent probes. The typical sample after heating to 100 °C for 15 min showed a maximum absorption peak near 480 nm, and a strong narrow peak of fluorescence emission at 530 nm. The FWHM of the emission peak was 42 nm, which indicated a narrow size distribution range of QDs. The quantum yield (QY) of the fluorescent probes was measured using Rhodamine 6 G as a standard [28, 35], and showed a high QY up to 75%.

The CMC-QDs fluorescent probes were directly imaged by transmission electron microscope (Philips, CM12) equipped with an Oxford EDX detector. The morphology analysis showed that the fluorescent probes were spherical and uniform in size (Fig. 7). The diameter of fluorescent probes was about 3.5 nm.

Figure 8 shows the X-Ray spectrum of the electron probe microanalysis (EPMA) of the CMC-QDs fluorescent probes. The X-Ray spectrum reveals the existence of sulfur, cadmium and tellurium in the fluorescent probe, implying that the QDs had an alloy shell of CdTe(S). The arrows indicated the location of characteristic peaks of sulfur, cadmium and tellurium, respectively. It is clear that the element sulfur as identified by X-ray in the shell is a breakdown product of mercaptoacetic acid used as sulfur source during microwave irradiation.

The MDCK cells were labeled with different concentrations of the CMC-QDs fluorescent probes. The average fluorescent intensities of the MDCK cells were measured with a FACSCalibur flow cytometer (Becton, Dickinson and Company, USA). after being cultured under the same conditions. The results are shown in Table 1. The average fluorescent intensity of MDCK cells increases markedly as the CMC-QDs incorporates into the cells. However the growth of the cells can be affected adversely by this incorporation process. When incubated with high concentrations (>0.25 mM) of CMC-QDs, some cells would not attach to the dish or even broke off and ruptured. The optimum concentration of CMC-QDs for MDCK cells was found to be around 0.1 mM in our experiments. At this concentration, the average fluorescence intensity of MDCK cells was relatively high and the growth of cells was not

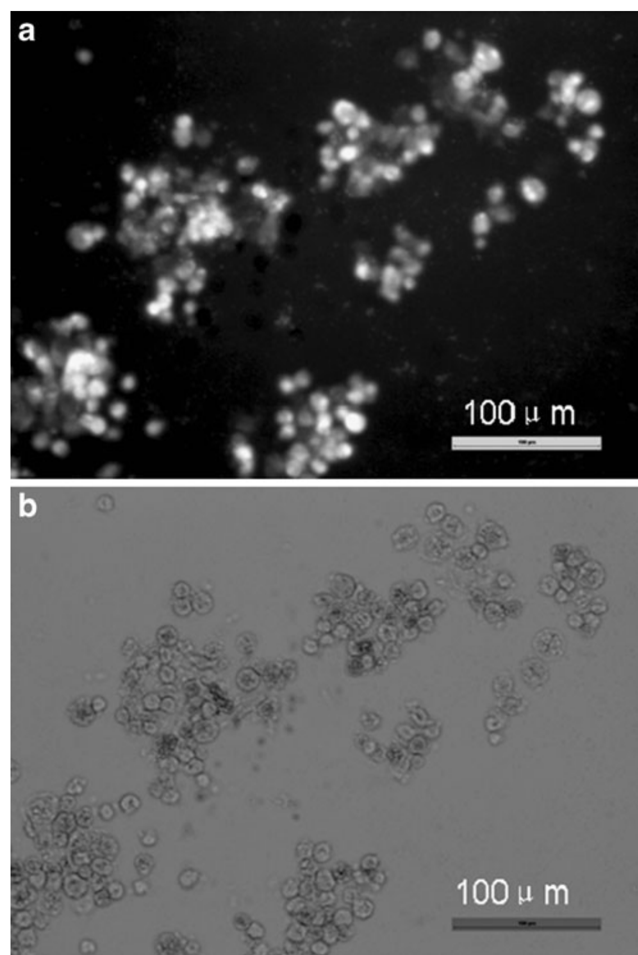

Fig. 9 Labeling of MDCK cells with green CMC-QDs (**a**: Fluorescence, **b**: bright field)

significantly affected. When incubated with live MDCK cells, CMC-QDs could be found inside the cells and emitted strong fluorescence (Fig. 9).

Conclusion

A method for microwave-assisted aqueous synthesis of CdTe/CdS QDs was optimized in this study. The QDs interacted with the CMC and CMC-QDs were assembled *via* chelation of amino and carboxyl groups in CMC with QD. The CMC-QDs had good uniformity in size, excellent fluorescence properties (FWHM=40-60 nm, quantum yield ≥75%) and relatively long period of stability (over 10 months at room temperature), compared with the unmodified CdTe/CdS QDs. With appropriate concentration (around 0.1 mM), the CMC-QDs labeled MDCK cells showed good fluorescent intensity in the cytoplasm and the CMC-QDs did not cause any visible damage to the cells or significantly inhibited their growth. This suggests that the CMC-QDs have good biocompatibility. With all these characteristics, CMC-QDs can be expected to find broad applications in life sciences, most noticeably in tracking the cells and their intracellular activities.

Acknowledgment This work was supported by National High Technology Research and Development Program 863 of China (No. 2007AA06Z418).

References

1. Vossmeyer T, Katsikas L, Giersig M, Popovic IG, Diesner K, Chemseddine A, Eychmueller A, Weller H (1994) CdS nanoclusters: synthesis, characterization, size dependent oscillator strength, temperature shift of the excitonic transition energy, and reversible absorbance shift. J Phys Chem 98(31):7665–7673
2. Rogach AL, Kornowski A, Gao M, Eychmüller A, Weller H (1999) Synthesis and characterization of a size series of extremely small thiol-stabilized CdSe nanocrystals. J Phys Chem B 103 (16):3065–3069
3. Zhang H, Wang LP, Xiong HM, Hu LH, Yang B, Li W (2003) Hydrothermal synthesis for high-quality CdTe nanocrystals. Adv Mater 15(20):1712–1715
4. Gaponik N, Talapin DV, Rogach AL, Hoppe K, Shevchenko EV, Kornowski A, Eychmüller A, Weller H (2002) Thiol-capping of CdTe nanocrystals: an alternative to organometallic synthetic routes. J Phys Chem B 106:7177–7185
5. Rogach AL, Katsikas L, Kornowski A, Su D, Eychmüller A, Weller H (1996) Synthesis and characterization of thiol-Stabilized CdTe nanocrystals. Ber Bunsenges Phys Chem 100:1772–1778
6. Li M, Ge Y, Chen Q, Xu S, Wang N, Zhang X (2007) Hydrothermal synthesis of highly luminescent CdTe quantum dots by adjusting precursors' concentration and their conjunction withBSA as biological fluorescent probes. Talanta 72:89–94
7. Kurth DG, Lehmann P, Lesser C (2000) Engineering the surface chemical properties of semiconductor nanoparticles: surfactant-encapsulated CdTe-clusters. Chem Commun 11:949–950
8. Wang C, Gao X, Su XG (2010) In vitro and in vivo imaging with quantum dots. Anal Bioanal Chem 397:1397–1415
9. Grisaru H, Palchik O, Gedanken A, Slifkin MA, Weiss AM, Palchik V (2003) Microwave-assisted polyol synthesis of CuInTe2 and CuInSe2 nanoparticles. Inorg Chem 42:7148–7155
10. Qian H, Li L, Ren J (2005) One-step and rapid synthesis of high quality alloyed quantum dots (CdSe/CdS) in aqueous phase by microwave irradiation with controllable temperature. Mater Res Bull 40:1726–1736
11. Song L, Duan J, Zhan J (2010) One-pot Microwave assisted synthesis of homogeneously alloyed $CdSe_xTe_{1-x}$ nanocrystals with tunable photoluminescence. Mater Lett 64:1843–1845
12. Liao XH, Chen NY, Xu S, Yang SB, Zhu JJ (2003) A microwave assisted heating method for the preparation of copper sulfide nanorods. J Cryst Growth 252:593–598
13. Grisaru H, Palchik O, Gedanken A, Slifkin MA, Weiss AM, Palchik V (2003) Microwave-assisted polyol synthesis of CuInTe2 and CuInSe2 nanoparticles. Inorg Chem 42:7148–7155
14. Palchik O, Zhu JJ, Gedanken A (2000) Microwave assisted preparation of binary oxide nanoparticles. J Mater Chem 10:1251–1254
15. Zhu JJ, Palchik O, Chen SG, Gedanken A (2000) Microwave assisted preparation of CdSe, PbSe, and Cu2-xSe nanoparticles. J Phys Chem B 104:7344–7347
16. Gao XH, Cui YY, Levenson RM, Chung LWK, Nie SM (2004) In vivo cancer targeting and imaging with semiconductor quantum dots. Nat Biotechnol 22:969–976
17. Alivisatos P (2004) The use of nanocrystals in biological detection. Nat Biotechnol 22:47–52
18. Michalet X, Pinaud FF, Bentolila LA, Tsay JM, Doose S, Li JJ, Sundaresan G, Wu AM, Gambhir SS, Weiss S (2005) Quantum dots for live cells, in vivo imaging, and diagnostics. Science 307:538–544
19. Howarth M, Takao K, Hayashi Y, Ting AY (2005) Targeting quantum dots to surface proteins in living cells with biotin ligase. Proc Natl Acad Sci 102:7583–7588
20. Lovric J, Bazzi HS, Cuie Y, Fortin GRA, Winnik FM, Maysinger D (2005) Differences in subcellular distribution and toxicity of green and red emitting CdTe quantum dots. J Mol Med 83:377–385
21. Lovric J, Cho SJ, Winnik FM, Maysinger D (2005) Unmodified cadmium telluride quantum dots induce reactive oxygen species formation leading to multiple organelle damage and cell death. Chem Biol 12:1227–1234
22. Muzzarelli R, Baldassarre V, Conti F, Ferrara P, Biagini G, Gazzanelli G, Vasi V (1988) Biological activity of chitosan: ultrastructural study. Biomaterials 9:247–252
23. Jigar MJ, Sinha VK (2007) Ceric ammonium nitrate induced grafting of polyacrylamide onto carboxymethyl chitosan. Carbohyd Polym 67:427–435
24. Wang PF, Wu SHK, Shi XY, Deng BM, Sun C (1998) The aggregation behavior of chitosan bioelectret in aqueous solution using a fluorescence probe. J Mater Sci 33:1753–1757
25. Xie WM, Xu PX, Wang W, Liu Q (2002) Preparation and antibacterial activity of a water-soluble chitosan derivative. Carbohyd Polym 50:35–40
26. Chen L, Du Y, Tian Z, Sun L (2005) Effect of the degree of deacetylation and the substitution of carboxymethyl chitosan on its aggregation behavior. J Polym Sci Polym Phys 43:296–305
27. Zhang H, Zhou Z, Yang B, Gao M (2003) The influence of carboxyl groups on the photoluminescence of mercaptocarboxylic acid-stabilized CdTe nanoparticles. J Phys Chem B 107:8–13
28. He Y, Sai LM, Lu HT, Hu M, Lai WY, Fan QL, Wang LH, Huang W (2007) Microwave-assisted synthesis of water-dispersed CdTe nanocrystals with high luminescent efficiency and narrow size distribution. J Chem Mater 19:359–365

29. He Y, Lu H, Sai L, Lai W, Fan Q, Wang L, Huang W (2006) Synthesis of CdTe nanocrystals through program process of microwave irradiation. J Phys Chem B 110:13352–13356
30. Wuister SF, Driel F, Meijerink A (2003) Luminescence and growth of CdTe quantum dots and clusters. Phys Chem Chem Phys 5:1253–1258
31. Bao H, Gong Y, Li Z, Gao M (2004) Enhancement effect of illumination on the photoluminescence of water-soluble CdTe nanocrystals: toward highly fluorescent CdTe/CdS core−shell structure. Chem Mater 16:3853–3859
32. Wang Y, Tang Z, Correa-Duarte MA, Pastoriza-Santos I, Giersig M, Kotov NA, Liz-Marzan LM (2004) Mechanism of strong luminescence photoactivation of citrate-stabilized water-soluble nanoparticles with CdSe cores. J Phys Chem B 108:15461–15496
33. Lin YW, Hsieh MM, Liu CP, Chang HT (2005) Photoassisted synthesis of CdSe and core−shell CdSe/CdS quantum dots. Langmuir 21:728–734
34. Aldana J, Wang A, Peng XJ (2001) Photochemical instability of CdSe nanocrystals coated by hydrophilic thiols. Am Chem Soc 123:8844–8850
35. Talapin DV, Rogach AL, Shevchenko EV, Kornowski A, Haase M, Weller H (2002) Dynamic distribution of growth rates within the ensembles of colloidal II–VI and III–V semiconductor nanocrystals as a factor governing their photoluminescence efficiency. J Am Chem Soc 124:5782–5790