Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 152 (2016) 343–351

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

The fluorescent interactions between amphiphilic chitosan derivatives and water-soluble quantum dots

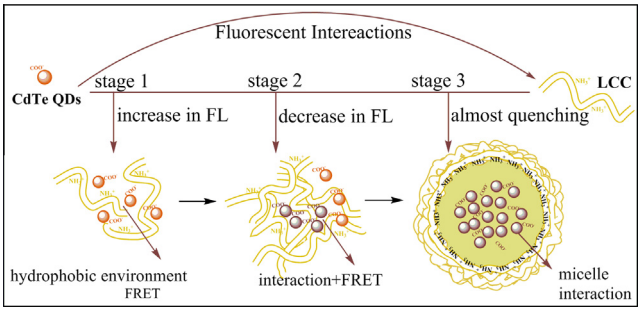
Xuening Fei [a,c], Miaozhuo Yu [b], Baolian Zhang [b,*], Lingyun Cao [a,*], Lu Yu [a], Guozhi Jia [a], Jianguo Zhou [a]

[a] Colleges of Science, Tianjin Chengjian University, Tianjin 300384, China
[b] School of Materials Science and Engineering, Tianjin Chengjian University, Tianjin 300384, China
[c] School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China

HIGHLIGHTS

- There were more than one kind of fluorescent interaction between chitosan derivatives and CdTe QDs were proposed.
- The inherent fluorescence of chitosan derivatives should not be ignored.
- There was a FRET effect between chitosan derivatives and CdTe QDs.
- The stability of QDs aqueous solution enhanced obviously.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 16 March 2015
Received in revised form 12 July 2015
Accepted 13 July 2015
Available online 14 July 2015

Keywords:
Amphiphilic chitosan
CdTe QDs
Encapsulation
Fluorescent interactions

ABSTRACT

The LCC–CdTe quantum dots (QDs) hybrid was fabricated by mixing the N-lauryl-N, O-carboxymethyl chitosan (LCC) micelle with water-soluble CdTe QDs in an aqueous solution via hydrophobic forces and the electronic attraction. The structures of LCC and LCC–CdTe QDs hybrid were determined by differential scanning calorimetry (DSC), Fourier transform infrared (FT-IR) spectroscopy and transmission electron microscopy (TEM). The results showed that the lauryl and carboxymethyl were successfully grafted to chitosan oligosaccharide (CSO), and a number of CdTe QDs were encapsulated by LCC micelle to form a core/shell structure. The tested results of the fluorescent characteristics of LCC, CdTe QDs and LCC–CdTe QDs hybrid showed that there were some obvious fluorescent interactions between LCC and CdTe QDs. Meanwhile, with the change in LCC space structure, the fluorescent interactions between LCC and QDs showed different fluorescent characteristics. The QDs fluorescent (FL) intensity increased first and then decreased to almost quenching, while LCC FL intensity decreased continually.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

The photoluminescent semiconductor quantum dots (QDs), due to their unique physico-chemical and optical properties, have attracted extensive interest in the biology field such as the fluorescent probe in biological staining, diagnostics and drug delivery [1–3]. Compared with organic dyes, the QDs seemed more promising in biological analysis because of their broad, tunable, stronger and narrower symmetrical emission spectrum and relatively stable photochemical properties. However, the traditional QDs with excellent optical properties are harmful to the biological species because the inevitable leakage of heavy metals severely affects the human health [4–7]. In addition, the thiol-quantum dot bonds are not very stable and, as a consequence, QDs begin to precipitate in the buffer solution and water over a long period

* Corresponding authors at: Tianjin Chengjian University, No. 26 Jinjing Road, Xiqing District, Tianjin, China.
E-mail addresses: feixuening123@163.com (B. Zhang), caolinyun54@126.com (L. Cao).

http://dx.doi.org/10.1016/j.saa.2015.07.068
1386-1425/© 2015 Elsevier B.V. All rights reserved.

of time [8]. The poor stability in aqueous solution also restricts the use of QDs in biological field. In order to overcome these disadvantages stated above, the encapsulation of QDs with biopolymers was an efficiency method [8,9].

In the encapsulation of QDs for bio-applications, the carbohydrates have advantages over other biological materials because of their biocompatibility, relative chemical solubility and stability in aqueous physiological environment [1,10–13]. And among these carbohydrates, chitosan is a promising biodegradable polymer to encapsulate QDs for the imaging of tumor and the visualization of drug distribution in vivo, [1,14,15] because the positively charged surface of the chitosan nanoparticles have strong interaction with the membrane of cancer cells for endocytosis [16–20]. Lin et al. [21] encapsulated CdSe/ZnS QDs with chitosan to prepare hybrid nanospheres (CS–QDs) by utilizing ethanol-aided counterion complexation in aqueous solution. The obtained CS–QDs hybrid nanospheres had not only loading space provided by the chitosan spherical matrix for loading multiply QDs, but also unique fluorescent properties provided by the encapsulated QDs. Moreover, these hybrid nanospheres possessed good biocompatibility and optical stability in physiological environment. Malhotra et al. [22] deposited the positive chitosan encapsulated CdTe QDs onto the indium-tin-oxide (ITO) coated glass substrates via electrophoretic deposition (EPD) technique, and the prepared nanostructure composite was found to detect target DNA in a wide concentration range. Additionally, the fabricated DNA biosensor could distinguish clinical samples of chronic myelogenous leukemia (CML) positive and negative patients. Yan et al. [23] synthesized the CS-ZnO Nanoparticles with a polymerization method in an aqueous solution using $Zn(NO_3)_2{\cdot}6H_2O$ as the precursor, and the hybrid nanospheres had obvious hollow structure that were expected to be simultaneously used as biological fluorescent labeling and a carrier for guest materials. Su et al. [16] fabricated a novel carboxymethyl chitosan-coated CdTe QDs (CMC–CdTe QDs) via the electrostatic interaction between amino groups in the carboxymethyl chitosan polymeric chains and carboxyl groups of the CdTe QDs. And the CMC on the surface of CdTe QDs had strong binding ability with Zn^{2+}, resulting in the obvious enhancement of the photoluminescence of CdTe QDs. The results indicated that the CMC–CdTe QDs was a robust and sensitive nanoprobe to detect intracellular Zn^{2+}. He et al. [14] investigated the interaction between CdSe QDs and chitosan with a Resonance Rayleigh Scattering (RRS) method, and the results showed that the chitosan and CdSe QDs formed a network structure aggregates by electrostatic attraction and hydrophobic force. In addition, after the interaction of CdSe QDs with chitosan, the intensities of RRS, Second-order Scattering (SOS), and Frequency Doubling Scattering (FDS) enhanced and the enhancements were in proportion to the concentration of chitosan. Also, they indicated that the increase of the molecular volume and the hydrophobic force between CdSe QDs-chitosan and water were the reasons for the RRS enhancement.

As mentioned above, the encapsulation with chitosan derivatives not only successfully enhanced the stability and biocompatibility of QDs but also reduced its biological toxicity. In addition, the reported results showed that there were some interactions between chitosan and QDs, which was potentially useful for further application in the bio-detection and labeling of biomolecules. However, there were few reports on the QDs fluorescent properties affected by the inherent fluorescence of chitosan [24].

In this work, we prepared a LCC–CdTe QDs hybrid by mixing the N-lauryl-N, O-carboxymethyl chitosan (LCC) micelle with water-soluble CdTe QDs in an aqueous solution under ultrasonic. The fluorescent characteristics of the LCC–CdTe hybrid solutions with different concentration of LCC and CdTe QDs were tested, and the results were used to investigate the fluorescent interactions between chitosan and QDs.

2. Experimental

2.1. Materials

All reagents were analytical grade or chemically pure products, and they are commercially available. CSO was purchased from Jinan Haidebei Marine Bioengineering Co., Ltd (Mw ⩽5000, deacetylation degree of 85%).

2.2. Methods

2.2.1. Synthesis of CdTe QDs

Water-soluble CdTe QDs was prepared at low temperature according to the reference [25]. It was described in detail as follows: under N_2 atmosphere, deionized water (5 mL) was added to Te powder (0.0638 g) and excessive $NaBH_4$ (0.0674 g) under magnetic stirring at room temperature. After 1 h, the colorless NaHTe solution was prepared. Under stirring the $CdCl_2$ solution of $CdCl_2{\cdot}2.5H_2O$ (0.228 g) dissolved in deionized water (50 mL) and TGA (200 μL) stabilizer were added, and then the pH value of the mixed solution was adjusted to 9–10 by the addition of 1 mol/L NaOH solution. The solution was deaerated by N_2 bubbling for 30 min, and the CdTe precursor was formed. Under reflux and oxygen-free condition the resulted mixture was heated at 90 °C for 170 min, precipitated with methanol, separated by centrifugation, re-dispersed in deionized diethyl ether twice and vacuum dried to obtain the CdTe QDs powder.

2.2.2. Synthesis of N-lauryl-N, O-carboxymethyl chitosan derivatives (LCC) [26]

2.2.2.1. Preparation of N-lauryl chitosan (LC). Briefly, chitosan (10.0 g) was suspended in 100 mL methanol with mechanical stirring at room temperature, and then lauraldehyde (4.87 g) was added (molar ratio of $-NH_2$:$-CHO$=1:0.5). After 24 h, $NaBH_4$ (5.0 g) dissolved in 10 mL cold water was slowly added to the solution. After a further 24 h continuous stirring, the reaction solution was neutralized with hydrochloric acid and the product was precipitated with methanol. Then the precipitate was filtered, repeatedly washed with methanol and water and dried in vacuum at 30 °C to obtain the light yellow N-lauryl chitosan.

2.2.2.2. Preparation of N-lauryl-N, O-carboxymethyl chitosan (LCC). 2 g N-lauryl chitosan and isopropyl alcohol were mixed in a 250 mL three-necked flask equipped a condenser, and then 9 g NaOH was added. After sonication for 5 min, the solution was heated at 40 °C and alkalified for 3 h with the help of mechanical stirring. Under sonication, 10 g chloroacetic acid was dissolved in isopropyl alcohol and drip into the mixture to react for 18 h. Then the supernate was separated and 40 mL deionized water was added to obtain a yellow transparent solution. The solution was adjusted to neutral with acetic acid, precipitated with methanol and filtered. Then the filter cake was washed with methanol/water solution (v/v = 90/10) for times, placed in the watch glass and vacuum dried at 30 °C for 3 h to obtain the white N-lauryl-O, N-carboxymethyl chitosan powder.

2.2.3. Preparation of LCC–QDs Hybrid solution

A series of aqueous LCC–QDs hybrid solutions were fabricated by adding LCC solutions with different concentration ranged from 0.001 to 1 mg/mL (0.001, 0.005, 0.01, 0.05, 0.1, 0.25, 0.5, 0.75, 1) to the aqueous QDs solution with a fixed concentration of 0.05 mg/mL, and then the mixture was sonicated for 30 min at

Download English Version:

https://daneshyari.com/en/article/1229781

Download Persian Version:

https://daneshyari.com/article/1229781

Daneshyari.com