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# Synthesis and characterization of poly(lactic acid)-conjugated CdTe quantum dots

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ABSTRACT

Novel poly(lactic acid)-conjugated CdTe quantum dots (PLA-conjugated CdTe QDs) were synthesized by surface grafting through living polymerization of lactic acid *O*-carboxyanhydride (LacOCA) on CdTe quantum dots. The PLA-conjugated CdTe QDs were spherical nanoparticle, and they were relatively uniform with a diameter of 4.5 nm. The PLA-conjugated CdTe QDs showed strong blue fluorescence emission in vitro, and their luminescence was stable in aqueous solution for more than 60 d. Furthermore, these QDs showed low cytotoxicity towards HaCaT cells in vitro. The results suggest potential applications for PLA-conjugated CdTe QDs in biological staining and diagnostics.



## 1. Introduction

Colloidal semiconductors, also known as quantum dots (QDs), have attracted intensive interest for applications in light-emitting devices [1,2], biological sensing [3], biological imaging [4,5], and photovoltaics [6]. CdTe QDs, which emit in the visible range, have been widely used for biological sensing and imaging, such as live-cell imaging [7,8] and cancer marker targeting [9,10]. However, because they release cadmium ions, CdTe QDs are highly cytotoxic, which has sparked much concern regarding their potentially adverse effects on the environment and human health [11]. To solve the problem of cytotoxicity, polymers are versatile surface modifiers because of their processability and tunable functionality [12]. Surface conjugation through living polymerization is one method for polymer modification of CdTe QDs. For example, QDs have been successfully incorporated into polystyrene particles with carboxyl groups by emulsion polymerization [13]. Poly(lactic acid) (PLA) is a biodegradable and biocompatible aliphatic polyester, approved by the United States Food and Drug Administration for clinical use, that can be produced either from direct polycondensation of lactic acid, or organocatalyzed ring-opening polymerization of lactide or lactic acid *O*-carboxyanhydride (LacOCA) [14].

In this study, we prepared PLA-conjugated CdTe QDs by surface grafting through living polymerization of lactic acid *O*-carboxyanhydride (LacOCA) on CdTe QDs. The modified CdTe QDs were characterized with regards to their size, fluorescence, and cytotoxicity.

## 2. Materials and methods

Synthesis of CdTe QDs: A 0.0293 g portion of $CdCl_2$, 0.4000 g of sodium citrate, and 0.0820 g of mercaptoethanol were dissolved into 35 mL of ultrapure water and adjusted to pH 7 with 1 M sodium hydroxide solution. The mixture was purged with nitrogen for 0.5 h to generate a clear homogenous liquor at room temperature. Then, 3 mL of the NaHTe aqueous solution (0.0076 g of tellurium powder and 0.0620 g of sodium borohydride) was added quickly under moderate stirring. This was followed by reflux for 151 h at 100 °C under moderate stirring. The QDs were precipitated by adding ethyl alcohol and then collected by centrifugation, washing, and drying at room temperature in vacuum for 24 h to yield a powder.

The synthesis of PLA-conjugated CdTe QDs: Briefly, 0.3 g of LacOCA and 0.3 g of as-prepared CdTe QDs were added into 30 mL of chloroform solution to remove the ethanol. 0.001 g of 4dimethylaminopyridine (DMAP) was used as a catalyst. The mixture was incubated at room temperature for 48 h. After polymerization, the PLA-conjugated CdTe QDs powder was precipitated by adding excess dry *tert*-butyl methyl ether, and filtered to get the PLA-conjugated CdTe QDs.

Characterization: UV–visible absorption and fluorescence spectra were performed at room temperature using Agilent 8453 UV–vis spectrometer (Agilent, USA) and RF-5301 fluorescence spectrometer (Shimadzu, Japan), respectively. Fourier transform infrared spectroscopy was performed on a FTIR-iS10 spectrometer (Nicolet, USA). The size and morphology were determined through a JEM-2100 transmission electron microscope (JEOL, Japan). The crystalline structure of the QDs was characterized by a D/Max-2200 X-ray diffractometer

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(Rigaku, Japan) with Cu *Ka* radiation. Cell culture and cell viability assay: HaCaT cells were tested by colorimetric 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyl tetrazolium bromide (MTT) assays [1].

## 3. Results and discussion

Scheme 1 illustrates the reaction to prepare the PLA-conjugated CdTe QDs. The hydroxyl groups of mercaptoethanol-stabilized CdTe QDs initiated the organocatalyzed ring-opening polymerization of LacOCA, which yielded PLA conjugated to the surface of the CdTe QDs. Successful surface conjugation was verified by FTIR spectroscopy [11].

Fig. 1a showed the UV–visible absorbance and fluorescence emission spectra of the CdTe QDs, and Fig. 1b showed the UV–visible absorbance and fluorescence emission spectra of the PLA-conjugated CdTe QDs. A blue-shift in both spectra becomes evident upon PLA conjugation, where the UV absorption peak changes from 545 nm to 390 nm, and the fluorescence emission peak changes from 570 nm (orange) to 415 nm (blue). The phenomenon of blue-shift originates from the quantum confinement effects [15]. The CdTe QDs exhibited fluorescence QY of up to 63.6%, while that of the PLA-conjugated CdTe QDs was up to 62.3%.

Fig. 1c shows the FTIR spectra of the CdTe QDs, the PLA, and the PLA-conjugated CdTe QDs. The broad absorption bands at 1268 and 3441 $cm^{-1}$ in the spectra of the CdTe QDs can be attributed to the $CH_2$–S– wagging vibration [16] and –OH stretching vibration, respectively. After conjugating PLA to the surface of the CdTe QDs, the absorption band of the C=O stretching vibration at 1746 $cm^{-1}$ appears in the FTIR spectrum of PLA-conjugated CdTe QDs, and the bands appearing at 1218 and 1369 $cm^{-1}$ correspond to C–O stretching and C–H bending vibrations, respectively. Meanwhile, the bending vibration peak of $–CH_3$ was observed at 1455 $cm^{-1}$. These characteristic peaks of PLA, appearing in the FTIR spectra of PLA-conjugated CdTe QDs, indicate successful conjugation of the PLA to the surface of the CdTe QDs.

TEM images showed that the CdTe QDs in ultrapure water easily formed aggregates, and the CdTe QDs were nearly spherical in shape with an average size of 3.5 nm (Fig. 2a). In contrast, TEM


**Scheme 1.** Schematic representation for the synthesis of the PLA-conjugated CdTe QDs.

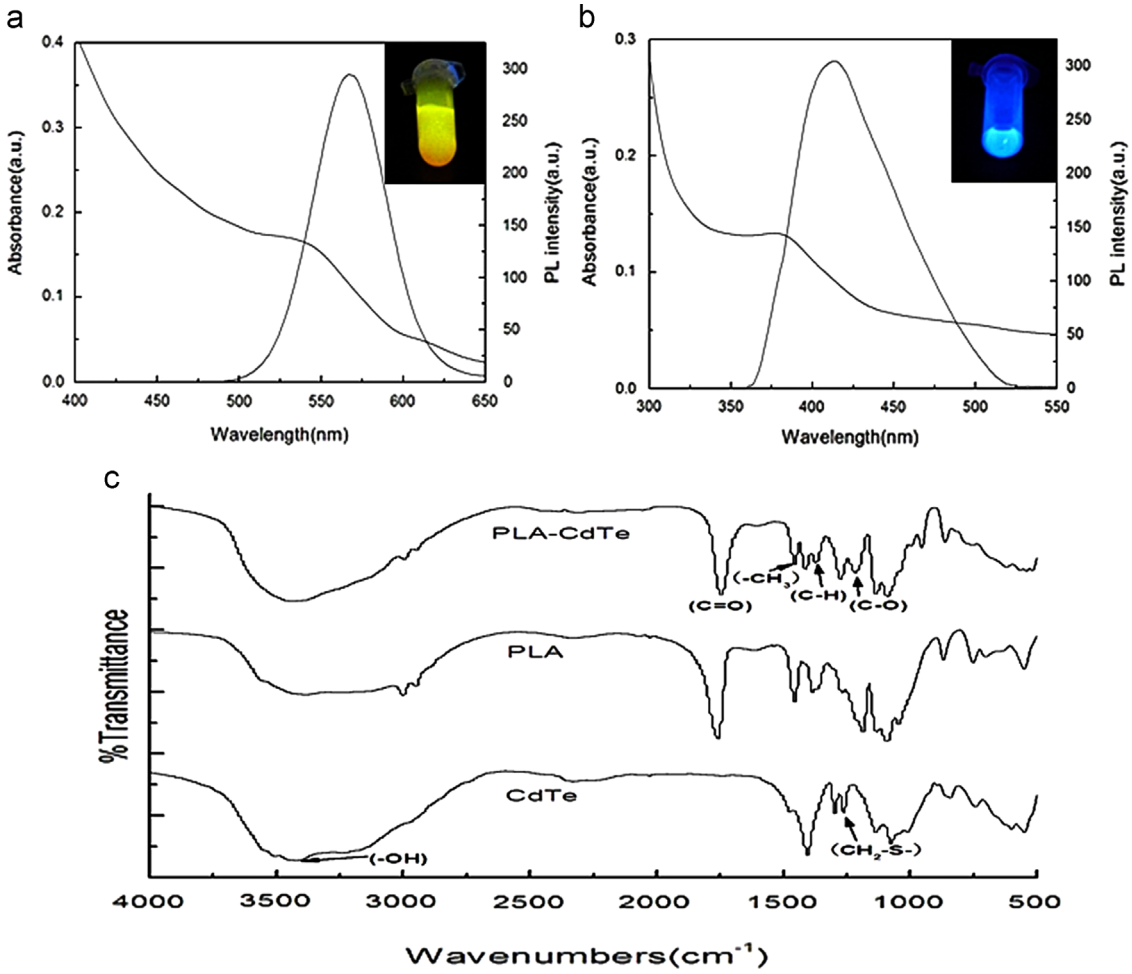


**Fig. 1.** UV-visible absorbance and Fluorescence spectra of (a) the CdTe QDs, and (b) PLA-conjugated CdTe QDs and (c) FTIR spectra of the CdTe QDs, PLA, and PLA-conjugated CdTe QDs.The inset showed fluorescent photograph of (a) the CdTe QDs and (b) PLA-conjugated CdTe QDs under UV irradiation. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)