Front. Optoelectron. 2013, 6(4): 452–457
DOI 10.1007/s12200-013-0345-7

RESEARCH ARTICLE

Preparation, structure and properties of fluorescent nano-CdTe/poly (1, 4–butanediol-citrate) bioelastomer nanocomposite *in-situ* dispersion technique

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Abstract Hydrophilic photoluminescent CdTe/poly (1, 4–butanediol-citrate) (PBC) bioelastomer nanocomposite was successfully synthesized by a two-step method and characterized by X-ray diffraction (XRD), Fourier transform infrared (FT-IR) spectroscopy, Uv-vis spectroscopy, photoluminescence (PL) spectroscopy and scanning electron microscope (SEM). The differential scanning calorimetry analysis shows that the bioelastomer nanocomposites with different mass fractions of CdTe have low glass-transition temperature, which indicates that they possess elastic property in the range from room temperature to the expected applied temperature (37°C). The measurements of the hydrophilicity, *in vitro* degradation and PL show that the nanocomposite has good hydrophilicity, degradation and high fluorescence properties.

Keywords bioelastomer, spectroscopy, biodegradable

1 Introduction

Recent years, semiconductor nanocrystals are interested in both fundamental research and technology applications, due to their unique properties [1–4]. It is found that the photoluminescence (PL) emissions of high-quality semiconductor nanocrystals usually have narrow full width at half maximum (FWHM), high photoluminescence quantum yields and strong penetrability. Fluorescent semiconductor nanoparticles have been extensively investigated in the past decade, and have been widely used as biolabels in imaging and biodetection. CdTe [5] was chosen because it is a representative example of the important luminescent semiconductor nanocrystals that has been used in numerous applications, such as in light-emitting devices, solar cells, integrated circuits and biological labels [6,7].

As a kind of important biodegradable material, polyester bioelastomer has been attracted widely attention [8,9] due to their stable three-dimensional network structure, excellent elastic and matched in human tissue and organ. They are good candidates for drug controlled carriers [10] and tissue engineering scaffolds [11].

Recently, there has been increasing attention on developing biodegradable materials with fluorescent properties [12]. Biodegradable photoluminescent polymers (BPLPs) with conjugating quantum dots have been reported in fluorescent-based biological applications, such as *in vitro* cellular labeling and *in vivo* cancer labeling.

However, as far as we know, the study on the photoluminescent bioelastomer with conjugating CdTe nanoparticles has not been reported. In this paper, we aim at the development of a novel CdTe/poly (1, 4–butanediol-citrate) (CdTe/PBC) bioelastomer nanocomposite with network structure, high photoluminescence and good hydrophilicity. And the preparation and fluorescent properties of the CdTe/PBC bioelastomer composite with different mass fractions of CdTe nanostructures are focused on.

2 Experiment

All of chemicals used for the synthesis were of analytical grade and used as received without any further purification.

Received May 23, 2013; accepted August 19, 2013

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2.1 Preparation of CdTe

Firstly, solution of Na_2TeO_3 (0.1 mmol) and $NaBH_4$ (1.7626 mmol) in 50 mL deionized water was placed in a three-necked round-bottom flask. The solution was heated to 80°C until the black precipitation disappeared. Then the Tellurium (Te) precursor solution must be cooled to the room temperature. The next step is $CdCl_2$ (0.2 mmol) and thioglycollic acid (0.1 mL) in 50 mL deionized water was adjusted to pH 10. The solution was placed in a 250 mL three-necked round-bottom flask, and then, the Te precursor solution was injected into the $CdCl_2$ solution system by stirring and kept heating at 80°C for 1 h. After cooling to room temperature naturally, a certain bulk ethanol was injected into the mixture solution. And then the obtained precipitates were separated by centrifugation, washed with deionised water followed by ethanol for three times, and dried at 60°C under vacuum for 24 h.

2.2 Preparation of CdTe/PBC bioelastomer composites

Citric acid (0.1 mol) and 1, 4–butanediol (0.75 mol) were added to a 100 mL three-neck round-bottom flask fitted with a distillation device. The mixture was kept dissolving under the protection of nitrogen gas by stirring at 140°C for 5 h by means of a silicone oil bath (reaction formula is shown in Scheme 1). Then the different additive amount (0.01, 0.02 or 0.03 g) of CdTe powder was adjusted to the 100 mL three-neck round-bottom flask by strring. And then it was kept at 110°C under vacuum for 4 h.

2.3 Charaterization

Fourier transform infrared (FT-IR) spectra were recorded on an AVATAR360 spectrophotometer using salt plates by hot-casting for the structure information. The X-ray diffraction (XRD) patterns were measured on a PANalytical X'pert diffractometer with Cu Kα radiation (λ = 1.54056 Å) for 2θ ranging from 5° to 90°. The glass-transition temperature was measured by DSC-204 phoenix. Hydrophilicity tests were measured by DropMaster300 to determine the water contact angle. The Uv-vis spectrum was taken from TU-1901 double beam Uv-vis spectrophotometer and the photoluminescence was carried out on a VARIAN fluorescence spectrophotometer with the excitation voltage of 600 V. Both the shape and the size of the prepared composite were characterized by scanning electron microscope (SEM) that was taken from Hitachi S-4800 operating at the accelerating voltage of 10 kV.

2.4 *In vitro* degradation

Disk specimen (10 mm in diameter approximately 1–1.5 mm thickness) was placed in a small bottle containing 20 mL phosphate buffer saline (pH 7.4). The bottle was incubated at 37°C for certain periods of time. After incubation, the film was washed with water and dried at 40°C in vacuum. Weight loss was calculated by comparing the initial mass (W_0) with the mass measured at a given time point (W_t), as shown in Eq. (1). There individual experiments were performed for degradation test, and then the average value was gained.

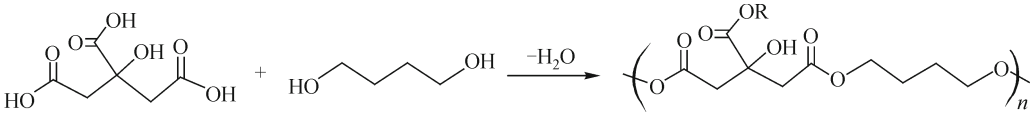
$$\text{Weight loss}(\%) = (W_0 - W_t)/W_0 \times 100\%. \quad (1)$$

3 Results and discussion

Figure 1 shows FT-IR spectra of the as-prepared PBC polymer and CdTe/PBC bioelastomer composite. The intense C=O stretch at 1731.42 cm^{-1} confirms the formation of ester bonds. FT-IR also shows a broad, intense-OH stretch at 3458.80 cm^{-1}. The peak at 2962.30 cm^{-1} was assigned to the flexing vibrating peaks of $–CH_2$, and the peak at 1402.02 cm^{-1} was assigned to the distortional vibrating peak of $–CH_2$. The bonds around 1194.07, 1165.23 and 1075.81 cm^{-1} were attributed to the C–O stretching absorption peak. The different intensity of peaks of 1402.02, 1194.07, 1165.23 and 1075.81 cm^{-1} in CdTe/PBC and PBC is due to the different content of PBC on salt plates.

The morphology of the CdTe/PBC bioelastomer composite is shown in Fig. 2. It can be observed that CdTe spheric nanoparticles with an average diameter about 200 nm are dispersed in PBC. The inset in Fig. 2 shows the appearance of the PBC polyester bioelastomer at room temperature, the color of PBC and CdTe/PBC bioelastomer composite are yellow and dark yellow, respectively, and both of them feel soft and smooth.

The differential scanning calorimeter (DSC) analysis curves of CdTe/PBC composites with different mass fractions of CdTe are shown in Fig. 3. It can be seen that the glass-transition temperature (T_g) of the CdTe/PBC composites with different mass fractions of CdTe was



Scheme 1 Reaction formula of condensing 1, 4–butanediol and citric acid (R = polymer chain)

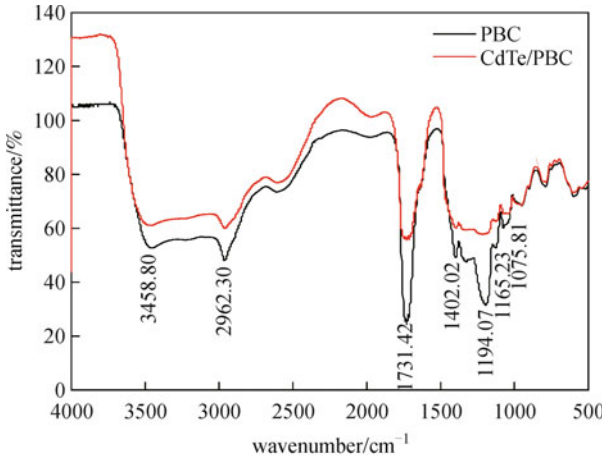


Fig. 1 FT-IR spectra of PBC pre-polymer and CdTe/PBC bioelastomer pre-composite

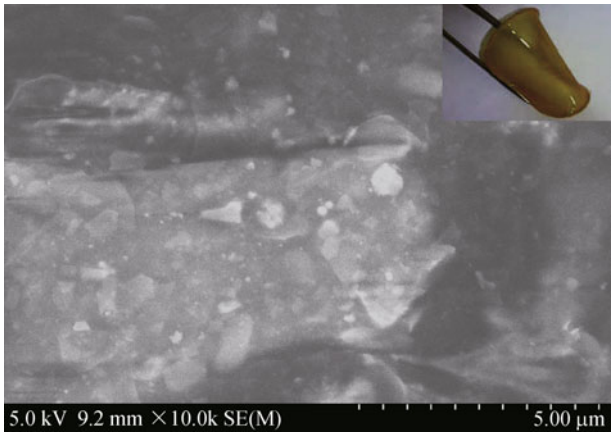


Fig. 2 SEM image of CdTe/PBC bioelastomer composite

about −18.4°C (0%), −18.6°C (0.067%), −21.9°C (0.121%), −26.2°C (0.0181%) respectively and was lower than room temperature; furthermore, we can see that the glass-transition temperature (T_g) decreases with the increase of the mass fractions of CdTe. Namely, the material has elasticity in a range from room temperature to expected applied temperature (37°C). Meanwhile, an exothermal peak is found in the crystallization of the blends or a curing exothermic peak, which is speculated that the material has certain ordered structures and the reaction of monomer is incomplete.

The XRD patterns of CdTe and CdTe/PBC bioelastomer composite with different mass fractions of CdTe (shown in Fig. 4) seem to confirm this conjecture. The XRD curve of pure PBC elastomer (0%) substrate has two dispersion peaks, which are 18.78° and 41.7°, respectively. The narrow and strong diffraction peak at $2\theta = 18.78°$ shows that pure PBC elastomer possess a certain ordered structure, which is contributed to the regular three-dimensional crosslinking network. With the increasing of the mass fractions of CdTe, the two dispersion peaks

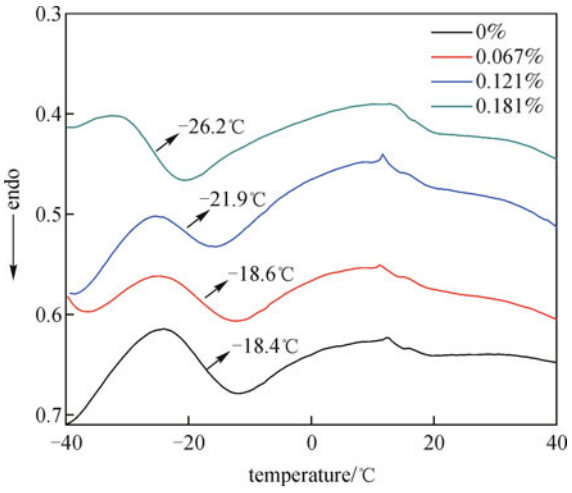


Fig. 3 DSC thermograms of CdTe/PBC composites with different mass fractions of CdTe

(18.78° and 41.7°) become wider and weaker, which may be due to the three-dimensionally ordered structure tridimentional affected by CdTe. Meanwhile, the XRD pattern of pure CdTe powder in Fig. 4 (the bottom black curve) shows three peaks at 24.41° (111), 41.2° (220) and 47.2° (311), conforming that CdTe has a cubic crystal structure.

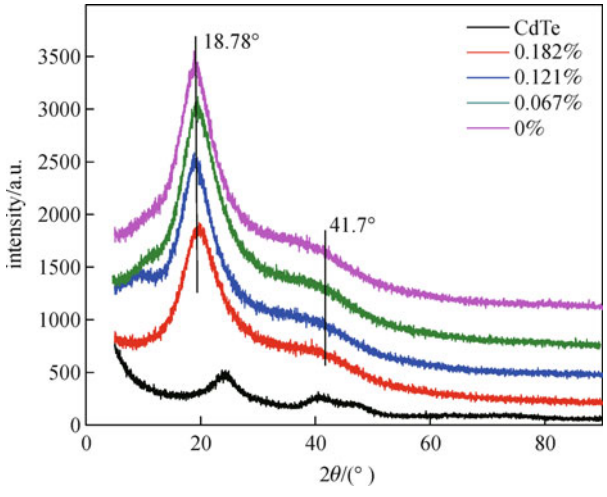


Fig. 4 XRD patterns of CdTe/PBC composites with different mass fractions of CdTe

Figure 5(a) illustrates the Uv-vis absorption spectrum (left) and PL spectrum (right) of the colloidal CdTe solution. The tangent to the ultraviolet absorption edge intersects with the wavelength coordinate axis at 350 nm, which exactly fits in with the excitation wavelength of the PL. The PL emission spectrum of colloidal CdTe solution covers the spectral region from 390 to 690 nm with a maximum locating at 528 nm. The shape of the PL spectrum is well-balanced without obvious trailing and has a narrow FWHM. The PL spectra of PBC (0%) and CdTe/

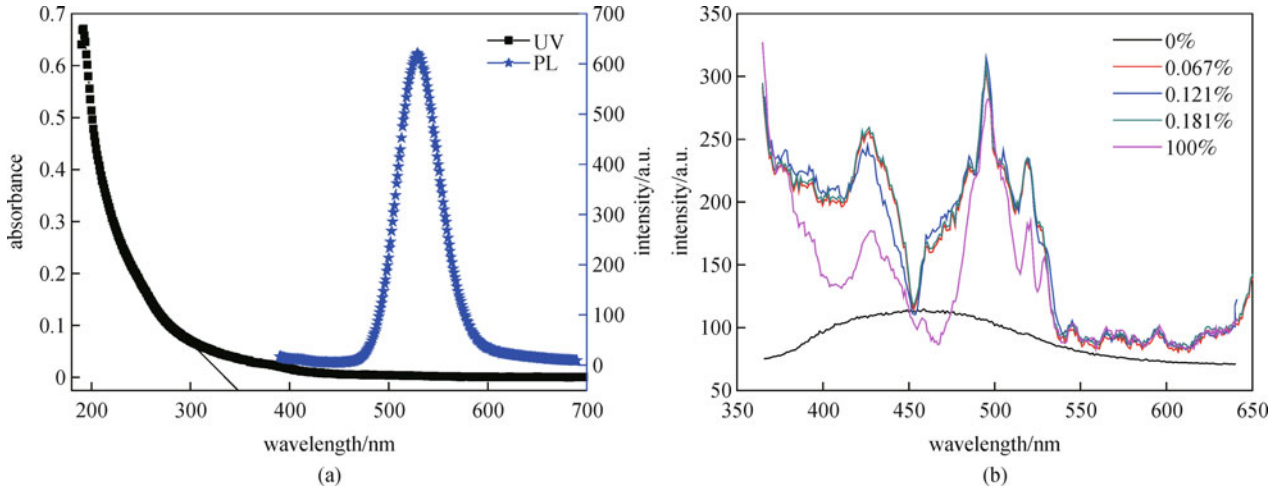


Fig. 5 Uv-vis absorption and PL spectra of colloidal CdTe (a); PL spectra of CdTe/PBC composites with different mass fractions of CdTe (b)

PBC bioelastomer composite measured with an excitation wavelength of 350 nm are displayed in Fig. 5(b). No fluorescence is detected in PBC elastomer, but CdTe/PBC bioelastomer composites show a high photoluminescence property. The maximum PL intensity of CdTe/PBC composite shifts to 495 nm and other two peaks appear at 425 and 519 nm, respectively, which indicates that CdTe has been introduced into PBC. Compared to the colloidal CdTe solution, the two shoulder peaks appearing in CdTe/PBC composite may be due to the enwrapped CdTe by PBC polymer and the surface defact. The photoluminescence intensity and shape of CdTe/PBC composites show little difference with the different mass fractions of CdTe, which indicates the stable of CdTe in PBC.

Water static contact angles allow us to characterize the hydrophilicity in the solid surface or film surface. The solid surface or film surface is hydrophilic, namely liquid wetting solid more easily, when θ is less than 90°. The smaller the angle is, the better hydrophilicity is. The solid surface or film surface is hydrophobic when θ is greater than 90°. And the liquid is not easy to wet on solid, but easy to move on the surface. Hydrophilicity tests were taken from PBC elastomer and CdTe/PBC bioelastomer composite, the results show that the water contact angle of the both is of 59° and 66° (Figs. 6(a) and 6(b)), respectively, which indicates that both of them have a good hydrophilicity.

In vitro degradation of the polymer and the composites is investigated by monitoring the change of the weight loss during degradation in phosphate buffer solution (pH 7.4). Figure 7 shows the weight losses of pure PBC (0%) bioelastomer and CdTe/PBC bioelastomer composites with different mass fractions of CdTe degraded in the phosphate buffer solution (pH 7.4) at 37°C. Generally speaking, the hydrolytic mechanism of materials involves bulk degradation and surface degradation. From Fig. 7, it can be seen that the weight loss of pure PBC (0%) increase rapidly with the degration time and about 20% after the first 8 hours, the fast degradation occurring in the early period might be caused by the quick degradation of the colloidal elastomer with low molecular weight, and then became correspondingly slower and stable in the latter period, the reason is due to the stable three-dimension network spatial structure. In the degradation process, the weight loss rate of pure PBC and the CdTe/PBC bioelastomer composites showed specific original kinetic in the initial duration, but it

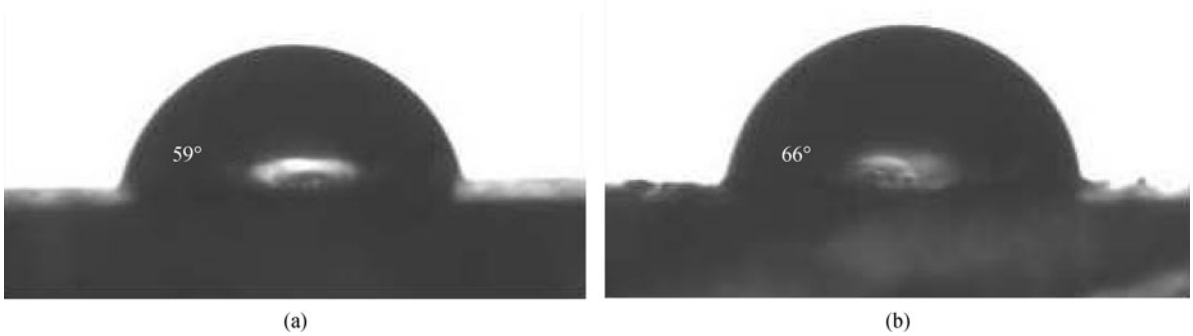


Fig. 6 Hydrophilic of PBC (a) and CdTe/PBC bioelastomer composite (b)

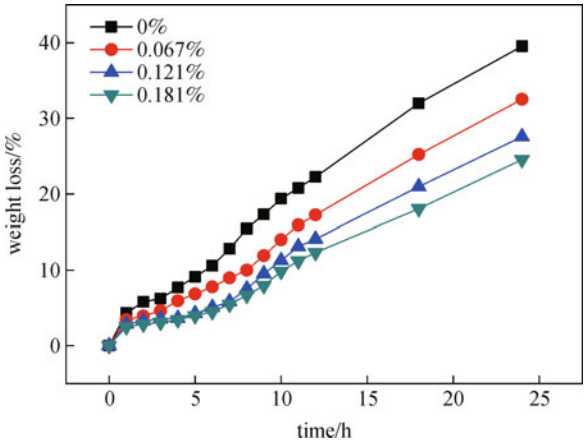


Fig. 7 *In vitro* degradation curves of CdTe/PBC composite with different mass fractions of CdTe

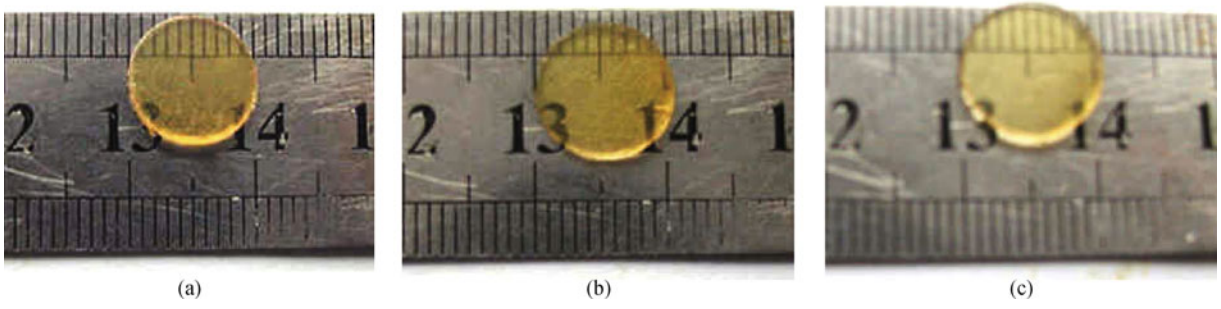


Fig. 8 Photos for CdTe/PBC composite placed in pH = 7.4 buffer solution for 0 h (a); 12 h (b); 24 h (c)

increased dramatically at last. The degradation rate of all the CdTe/PBC bioelastomer composites decreases gradually with the increase of mass fractions of CdTe. The degradation rate with mass fractions of CdTe of 0%, 0.067%, 0.121% and 0.181% is 39.53%, 32.52%, 27.57%, 24.53%, respectively. These results indicate that it is possible to manipulate the substrates and the composites degradation properties by altering the additive amount of CdTe.

Figure 8 demonstrates photos of CdTe/PBC composite with mass fractions of CdTe of 0.181% placed in pH = 7.4 buffer solution for different time in order to track the morphology changes in the process of experiment. From the photos in Fig. 8, it can be seen that CdTe/PBC composite soaking in buffer solution for 24 h, the size remains unchanged except that the thickness decreases, which indicates that the dimensions of composite materials are stabilized and makes them possible to use in biological tissue engineering as scaffold materials and other biomedical applications.

4 Conclusions

The thermosetting network, degradable and photoluminescent CdTe/poly (1, 4–butanediol-citrate) bioelastomer nanocomposite was successfully synthesized by a two-step method *in-situ* dispersion technique. The bioelastomer nanocomposite possesses elastic property in the range from room temperature to the expected applied temperature, good hydrophilicity, degradation and high fluorescence properties. This material is expected to be useful in soft tissue engineering with the function of fluorescence biomarker.

Acknowledgements This work was supported by the National Natural Science Foundation of China (Grant Nos. 21063005, 50968005 and 51163003), and the Scientific Research Foundation for the Returned Overseas Chinese Scholars, State Education Ministry (No. 20091341).

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