Preparation of Electrospun CdSe-Quantum-Dots-Doped Porous Films

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Abstract: Electrospun porous films doped with the green-synthesized CdSe quantum dots were synthesized. Glycerol was chosen to prepare the quantum dots (QDs), with the highest quantum yield of 78.28%. Polycaprolactone (PCL) was electrospun with CdSe QDs to avoid the QDs´ toxicity and improve the QDs´ cytocompatibility. The electrospun QDs-doped films preserve the original QDs´ fluorescence. Pores can be detected from the SEM of the films, predicting the possibility of loading drugs in the cancer therapy. The cell proliferation assay shows excellent cytocompatibility of the eletrospun CdSe-QDs-doped films. The present eletrospun CdSe-QDs-doped porous films are cytocompatibale, highly-fluorescent and potential to load drugs in cancer therapy.

Key words: *CdSe quantum dots (QDs); electrospun films; polycaprolactone (PCL); photoluminescence (PL); cytocompatibility; cell proliferation assay*

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Introduction

Early detection of cancerous cells is critical to rapidly initiate treatment and consequently increase patient survival [1-2]. Optical *in vivo* imaging is an easy and cost-effective way while providing rapid diagnosis with high resolution and physiological information about the issue, which could be used for the early detection of a developing cancer [3-4].

Recently, nanotechnology-based treatments are aggressively being explored in an effort to improve the efficiency and accuracy of cancer diagnosis while providing highly specific, and highly efficient cancer therapeutics. Semiconductor quantum dots (QDs) have been of interest for *in vivo* imaging largely due to their intense fluorescence emissions [5-7]. The size-tunable optical properties of QDs allow for the different band-gap and emission wavelength. In addition, QDs exhibit high quantum yields, sharp emission spectra, and a high resistance to photo-bleaching [8]. Lots of work about the QDs applied in optical *in vivo* imaging, such as CdSe, CdTe, CdSe/ZnS and InGaP QDs, has been reported [9-11]. However, overcoming severe side effects arising from the use of QDs with toxicity *in vivo* imaging and increasing the ability to deliver drugs to cure cancerous cells are key challenges in cancer therapeutics.

Since Reneker and co-workers developed new interest of electropsinning in 1990s for fabrication of nanofibers, it has turned into a versatile and effective technique due to its comparatively low manufacturing cost, large surface areas, and a three-dimensional porous structure predicted to be the drug carrier for rapid and sensitive bio-probe applications [12-16]. For novel bio-identification [17-23], growing efforts have been made to integrate QDs into electrospun fibers to achieve the excellent photochemical stability, emissive photoluminescence (PL), high cytocompatibility and good reproducibility, which are derived from the parent compositions of QDs and electrospinning [24-30]. Such electrospun CdSe QDs/polymer emissive porous films would ideally be porous for the loading of the therapeutics, nontoxic for the polymer blending with CdSe QDs and functionalized with fluorescent materials for ease of detection to the cancerous cells.

In this paper, the multifunctional nanocarriers of the electrospun CdSe-QDs-doped porous films were prepared and the cell proliferation on films was investigated. Furthermore, the cell live-dead staining graphs are presented. The as-described films would be cytocompatibale, highly fluorescent and porous to load drugs. Figure 1 is the schematic diagram of this idealized nanocarrier system for cancer treatment and diagnosis.

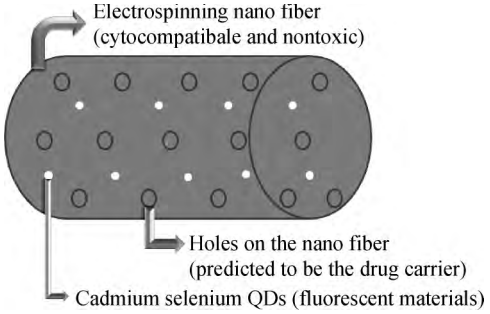

Fig. 1 Schematic diagram of an idealized nanocarrier system for cancer treatment and diagnosis

1 Experimental

1.1 Preparation of CdSe QDs

The Se precursor for the present work was prepared by mixing the selenium powder (0.005 mol) (AR, Shanghai Meixing Chemical Co., Ltd., China), sodium sulfite (0.01 mol) (AR, Sinopharm Chemical Reagent Co., Ltd., China), sodium hydroxide (0.01 mol) (AR, Shanghai Aijian Ready-Made Reagent Co., Ltd., China) and deionized water (50 mL) with N_2 protection and magnetic stirring. The mixture was heated to boiling while the solution turned from red brown to the black precipitated. Then sodium hydroxide (0.01 mol) was added, and after returning for 4 h, the reactants were cooled down to the room temperature followed by nitrogen protection for 30 min.

The Cd precursor was prepared by mixing glycerol and oleic acid (AR, Jiangsu Yonghua Fine Chemicals Co., Ltd.,

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China) together in volume ratio of 40∶8. Cadmium acetate 0.001 mol (AR, Sinopharm Chemical Reagent Co. Ltd., China) and sodium hydroxide (0.7 g) were added as precipitation agents to the mixed solvent (48 mL). The mixture was under N_2 protection until it became clear and transparent.

The CdSe QDs were synthesized by adding 10 mL Se precursor solution to the 48 mL Cd precursor solution, under N_2 protection and magnetic stirring. The reactions were carried out at 50, 70, 140, 170, and 200 ℃, for 5, 10, 15, 20, and 25 min, respectively.

1.2 Preparation of CdSe QDs/polymer blending solution for electrospinning

The as-prepared CdSe QDs were precipitated by adding ethanol into the reaction mixture and isolated by centrifugation. Then, the CdSe QDs were redissolved in polycaprolactone (PCL, Sigma-Aldrich, Co., USA) and chloroform (AR, Shanghai Lingfeng Chemical Reagent Co., Ltd., China) solution with the concentration of 20% by weight per mL (PCL/chloroform) for electrospinning. The concentration of the CdSe QDs in the electrospinning soulution was 0.10 mol/L. After vigorous stirring for 1 h at 28 ℃, the CdSe QDs were miscible with PCL and chloroform solution.

1.3 Electrospinning

The electrospinning apparatus was made up of three parts: a high voltage source, a syringe pump with spin needle, and a metal collector. The needle was placed vertically above the collector. The distance from the needle tip to the collector was 15 cm. The polymer solution is forced through a syringe pump, which is used to drive the polymer solution into the needle and to control the feed rate of 0.5 mL/h, forming a pendent drop at the tip of capillary. When the applied electric field of 12 kV (between the needle tip and the grounded collecting electrode) overcomes the surface tension force and viscoelastic force of the droplet, the polymer solution becomes stretched to form fibers upon volatilization of solvents toward the collecting electrode (the aluminum foil collector). Thus the CdSe QDs/PCL nanofibers were collected.

1.4 Cell isolation and culture

Human dermal fibroblasts (HDFs) were isolated and cultured from the superficial layer of adult human skin dermatomed at a depth of 400 μm according to previously described in Ref. [31]. HDFs below passage 10 were used for all studies. Dulbecco's modified eagle's medium (DMEM) with 10% fetal bovine serum (FBS) were used as HDF's culture medium.

1.5 Cell proliferation assay and live-dead staining

To determine the cytocompatibility of the electrospun CdSe-QDs-doped porous film on HDFs proliferation, the cell proliferation on the electrospun films doped with CdSe QDs (synthesized under 50, 70, 140, 170, and 200 ℃ for 25 min, respectively) were assayed for 1, 3, and 7 d, respectively. The HDFs were seeded in 96-well plates at 4×10^3 cells per well and cultured in a humidified 37 ℃/5%, CO_2 incubator. A CCK-8 assay (Cell counting kit-8, Dojindo, Kumamoto, Japan) was performed according to the manufacturer's instructions. At the end of the culture, the cells were stained with a live-dead viability cytotoxicity kit (Invitrogen), according to the manufacture's instruction to confirm their viability using ethidium homodimer and calcein-AM regents.

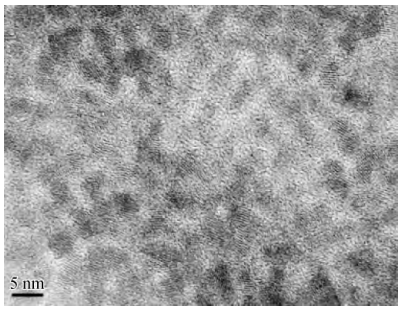
1.6 Characterization

The high resolution transmission electron microscopy (HRTEM) (JEM-201, American FEI company) was used to characterize the morphology of the samples. The optical absorption spectra (Lambda 950 UV-Visible Spectrophotometer, Perkin Elmer, Waltham, MA, USA) and the photoluminescence spectra (model Fluorolog-3-P, France Jobin Yvon Company; model Cary 500, American Varian Company) were measured for the calculation of CdSe QDs' quantum yield (QY) according to the absorption coefficient and integrated emission area. The morphology of the pure electrospun film and the CdSe QD/PCL composite porous film and energy dispersive X-ray spectroscopy (EDS) are evaluated by SEM (Bruker S-4800, with high voltage of 14.3 kV and pulse of 47.43 kcps). The cell proliferation was assayed by the absorbance of the cells cultured on the electrospun CdSe-QDs-doped films and measured spectrophotometrically using a microplate reader (Bio-Rad Benchmark Plus) at wavelengths of 450 nm with a reference wavelength of 650 nm. Cells on the electrospun CdSe-QDs-doped films were photographed at 100 times from five random microscopic fields using an upright fluorescence microscope (Leica DM 4000, Germany).

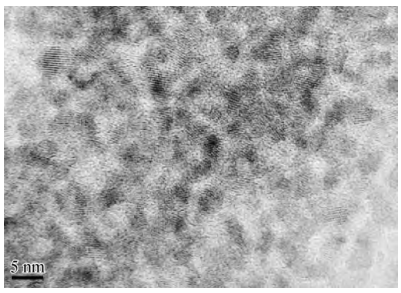
2 Results and Discussion

2.1 The morphology of the CdSe QDs

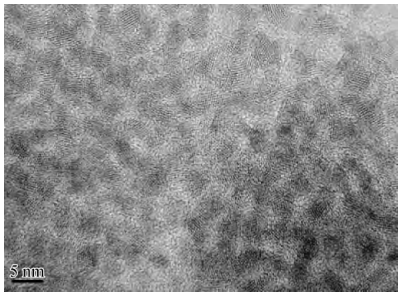
HRTEM photos of CdSe QDs under 50, 70, 140, 170, and 200 ℃ reacted for 25 min are presented in Fig. 2. It is seen that an excellent monodispersity of oval-shaped CdSe QDs is obtained with the size of 2.51, 2.71, 2.81, 2.94, and 3.11 nm, respectively. The existence of lattice fringe indicates that the products have excellent crystallinity.



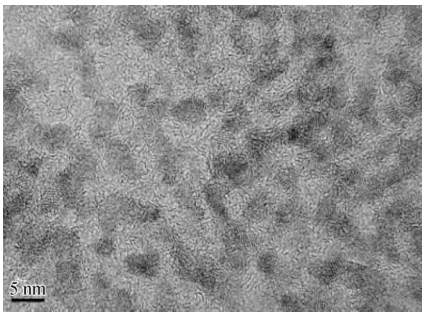
(a) 50 ℃



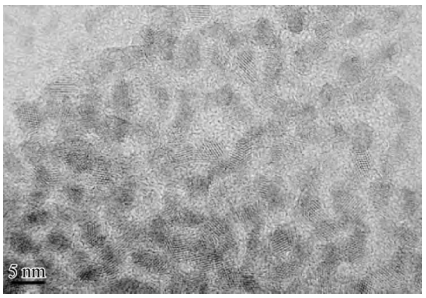
(b) 70 ℃



(c) 140 ℃



(d) 170 ℃



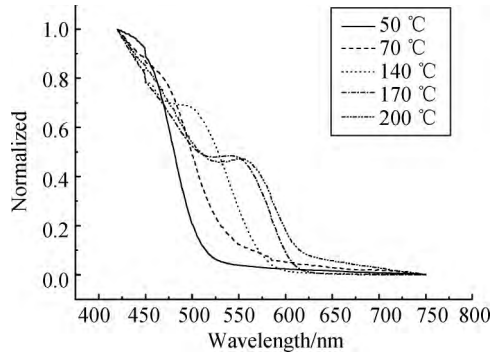
(e) 200 ℃

Fig. 2 HRTEM photos of CdSe QDs under 50, 70, 140, 170 and 200 ℃ in 25 min, respectively

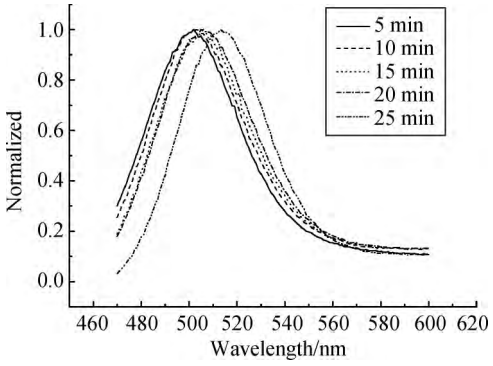
2.2 Absorption and PL spectra of the CdSe QDs

Figure 3 (a) shows the normalized absorption spectra of CdSe QDs reacted at 50, 70, 140, 170, and 200 ℃ for 25 min, respectively. It is seen that absorption peaks appear red shift from 450 to 570 nm with the increased reaction temperature, while comparing with that of the bulk CdSe (717 nm), an obvious blue shift occurs. These phenomena indicate occurrences of the band-gap narrowing and broadening, respectively, as a consequence of the quantum size effect. This tunable band-gap of CdSe QDs is suitable to be applied in *in vivo* imaging for multi-channel detection for the cancer therapy [4].

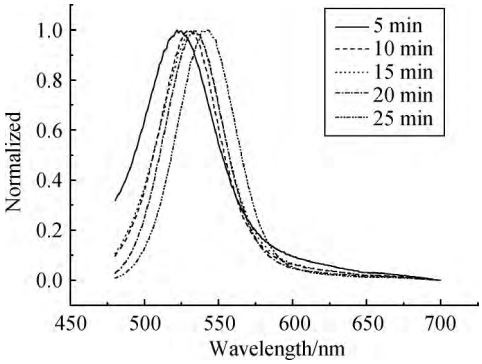
Figures 3(b)-(f) show the normalized emission spectra of CdSe QDs reacted at 50, 70, 140, 170, and 200 ℃ for 5, 10, 15, 20, and 25 min, respectively. Under the excitation of blue light (460 nm), a broad emission band is observed with the emission wavelength covering from 495 to 595 nm. Similar to absorption spectra above, the emission band shows an obvious red shift with the increasing reaction temperature and time, and it is also due to the quantum size effect.



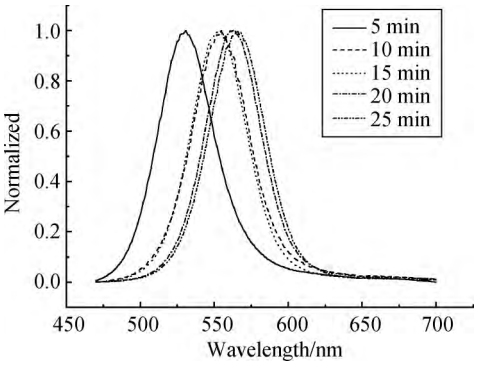
(a) Absorption spectra (for 25 min)



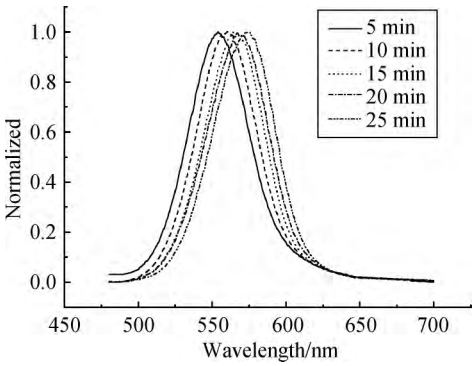
(b) 50 ℃



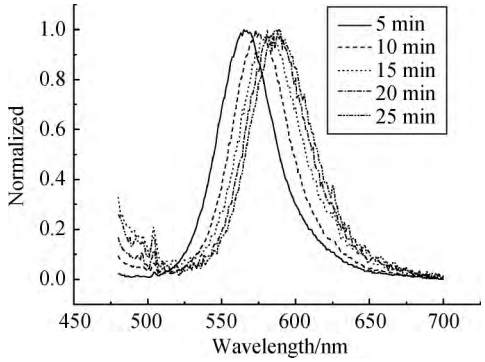
(c) 70 ℃



(d) 140 ℃



(e) 170 ℃



(f) 200 ℃

Fig. 3 Normalized absorption (a) and emission spectra (λ_{ex} = 460 nm, (b)-(f)) of CdSe QDs at 50, 70, 140, 170, and 200 ℃, for 5, 10, 15, 20 and 25 min, respectively

2.3 The calculated QY of CdSe QDs

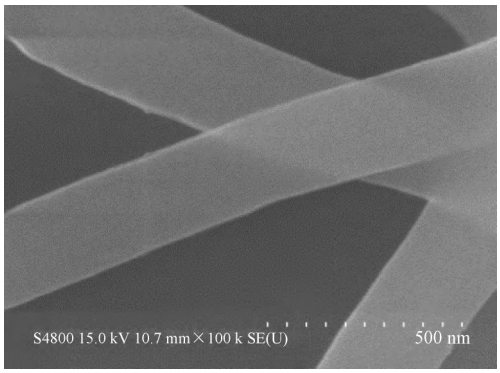
It is known via previously reported work that QY of CdSe QDs (reacted at 50, 70, 140, 170, and 200 ℃ for 25 min) can be calculated according to the following formula with rhodamine B as reference object [32-33]:

$$Y_Q = Y_R \cdot \frac{I_Q}{I_R} \cdot \frac{A_R}{A_Q} \cdot \left(\frac{N_Q}{N_R}\right)^2, \quad (1)$$

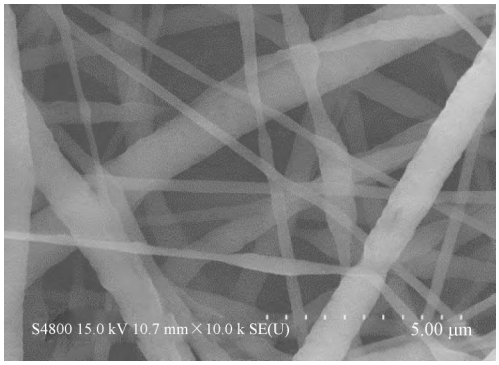
where Y_R is the standard QY (95%) of rhodamine B; I_Q and I_R represent the integral emission areas of CdSe QDs and rhodamine B under 460 nm excitation, respectively; A_R and A_Q are the absorption coefficients (around 0.05 or less than 0.05) of the rhodamine B and CdSe QDs at 460 nm [34-35]; and N_Q and N_R are refractive indices of the *n*-hexane (1.375) and ethanol (1.362) used as the solvents for the CdSe QDs and rhodamine B. The calculated QYs of the QDs synthesized at 50, 70, 140, 170, and 200 ℃ for 25 min, is 78.28%, 57.78%, 51.69%, 18.72%, and 26.92%, respectively.

2.4 SEM and EDS of the electrospun CdSe-QDs-doped porous films

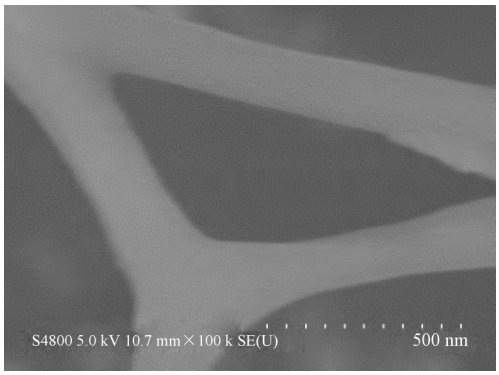
The SEM patterns of blank and QDs-doped electrospun films under 50, 70, 140, 170, and 200 ℃ for 25 min are shown in Figs. 4 (a)-(l), respectively. The diameter of nanofibers is around 200 nm for the blank films Figs. 4 (a)-(b) and decreases to 150 nm after QDs doping Figs. 4 (c)-(l). However, the addition of CdSe QDs did not affect the morphology of the original nanofibers. This electrospun CdSe QDs-doped film was also characterized using EDS (Fig. 4(m)) which confirmed the presence of the QDs in the film.



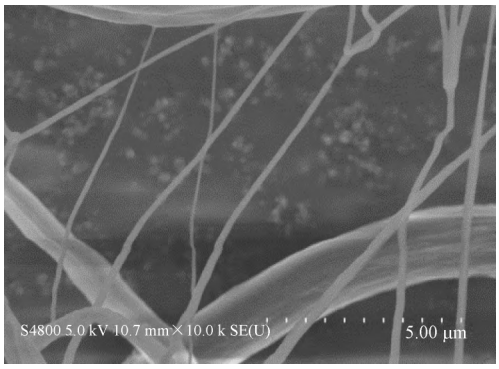
(a) Blank film (scale bar 500 nm)



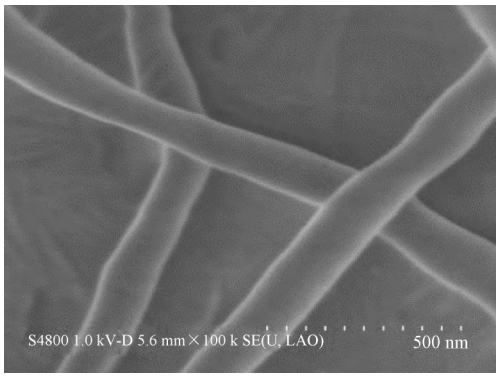
(b) Blank film (scale bar 5 μm)



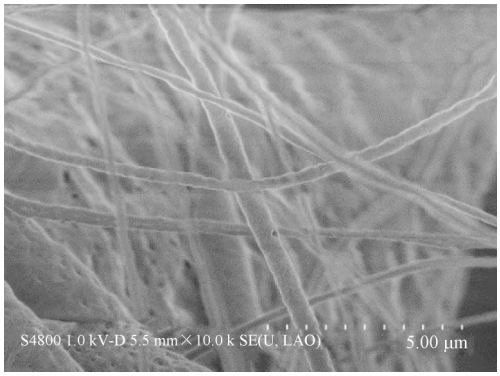
(c) Film with 50 ℃ QDs (scale bar 500 nm)



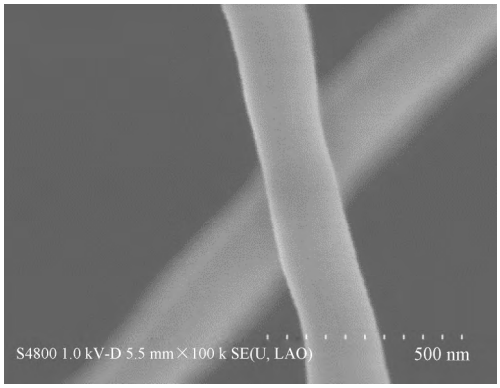
(d) Film with 50 ℃ QDs (scale bar 5 μm)



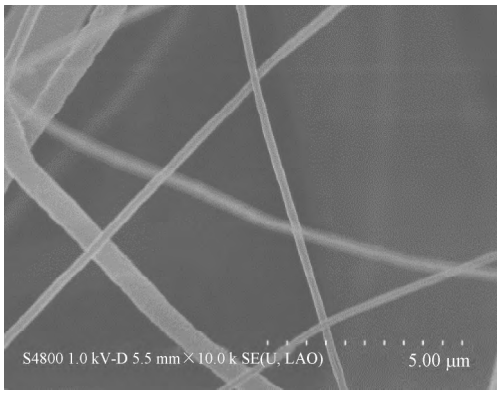
(e) Film with 70 ℃ QDs (scale bar 500 nm)



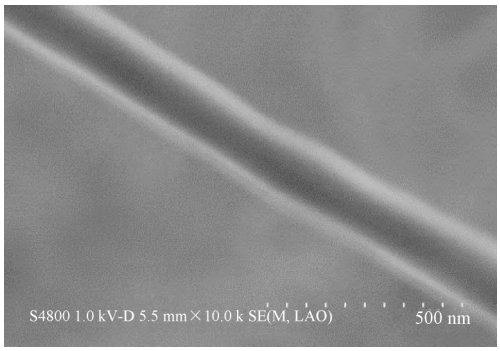
(f) Film with 70 ℃ QDs (scale bar 5 μm)



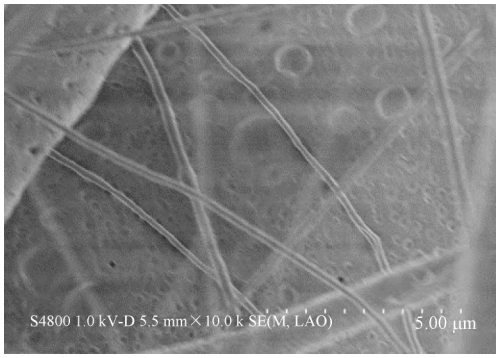
(g) Film with 140 ℃ QDs (scale bar 500 nm)



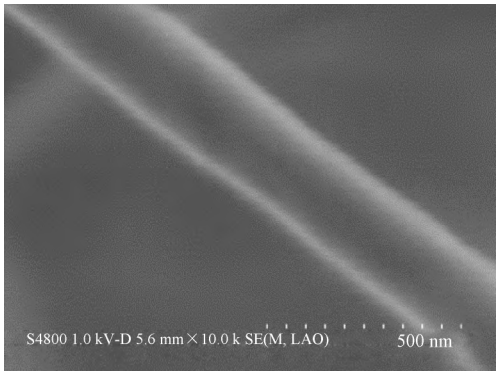
(h) Film with 140 ℃ QDs (scale bar 5 μm)



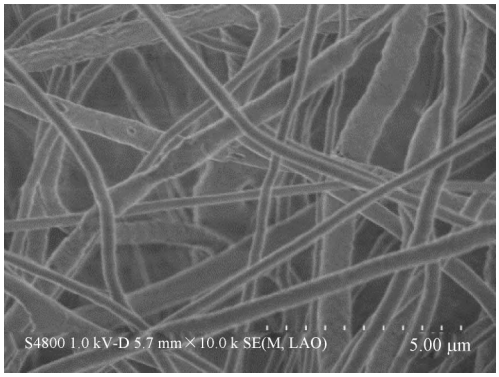
(i) Film with 170 ℃ QDs (scale bar 500 nm)



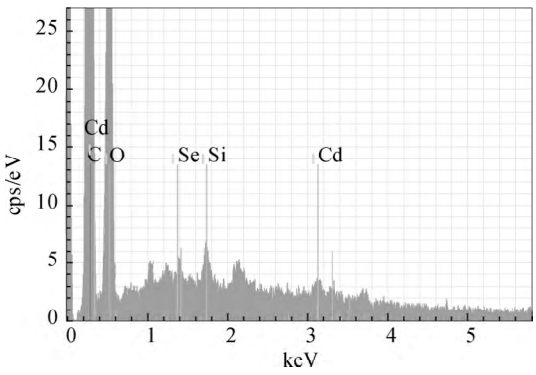
(j) Film with 170 ℃ QDs (scale bar 5 μm)



(k) Film with 200 ℃ QDs (scale bar 500 nm)



(l) Film with 200 ℃ QDs (scale bar 5 μm)



(m) EDS spectra of QDs-doped composite films (at 50 ℃ for 25 min)

Fig. 4 SEM patterns of blank films ((a) and (b)), QDs-doped films ((c)-(l), at 50, 70, 140, 170, and 200 ℃ in 25 min, respectively) and EDS spectra of the QDs-doped films ((m), at 50 ℃ for 25 min)

2.5 The PL spectra of the electropun CdSe QDs-doped porous films

Figure 5 presents the PL spectra of the electrospun CdSe QDs/PCL porous films (the QDs were synthesized at 50, 70, 140, 170, and 200 ℃ for 25 min, respectively) where the spectrum of the blank electrospun nanofibers is included as reference for comparison. It is obvious that the QDs-free films exhibit no fluorescence while the addition of CdSe QDs endows the films with the original CdSe QDs´ emissions in the region from 510 to 580 nm, depending on the reaction temperature, which is useful in the bio-identification in cancer diagnosis.

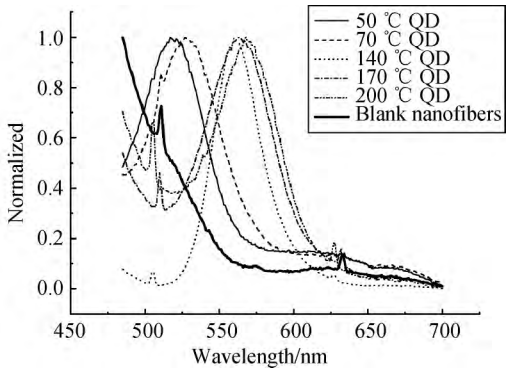


Fig. 5 The PL spectra of the electrosun CdSe QDs/PCL composite film (at 50, 70, 140, 170, and 200 ℃ for 25 min and blank nanofibers)

2.6 The cell proliferation assay and live-dead staining characterization

The cell proliferation assay is characterized by the bar chart as shown in Fig. 6 with cell proliferation for 1, 3 and 7 d, respectively. Cells grow well both on the blank and CdSe-QDs-doped electrospun films, although the absorbance of the cells cultured on the doped films decreases a little, comparing with the blank electrospun films. Furthermore, the QDs synthesized at 170 ℃ has the highest absorbance among all QDs-doped films. It should be highlighted that cell proliferation results show that the addition of the CdSe QDs don't affect the cell proliferation greatly and the electrospun CdSe-QDs-doped porous films has cytocompatibility, which is potential for application in the cancer therapy.

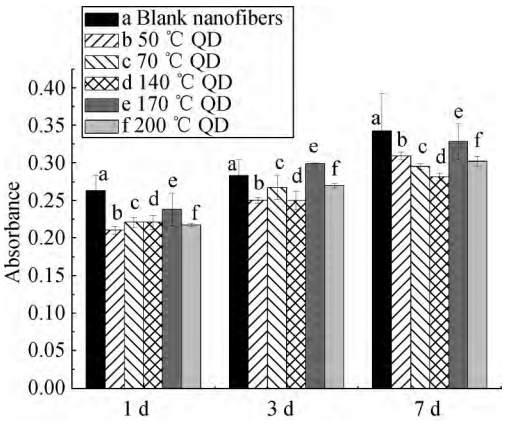
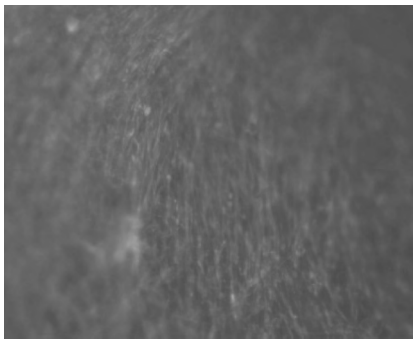
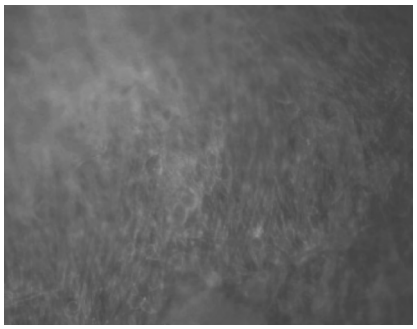


Fig. 6 The absorbance of the cells cultured for 1, 3, and 7 d, on the electrospun CdSe-QDs-doped films

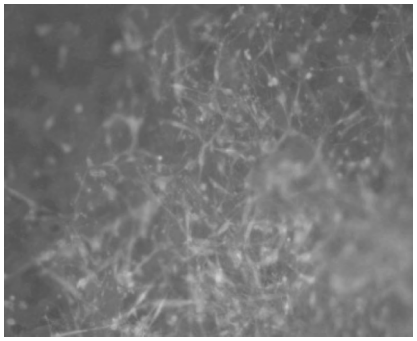
Figures 7 (a)-(f) show the real PL graphs of the cells cultured on the films without QDs (a) and doped with QDs (synthesized at 50, 70, 140, 170 and 200 ℃ for 25 min, (b)-(f), respectively), under excitation light of 450 nm. From Fig. 7 (a), the fusiform green cells can be seen clearly. Because the composite films preserve the original CdSe QDs´ fluorescence in the region from 510 to 580 nm, the punctate QDs emit the green to yellow light, which is similar to the PL of the cell.



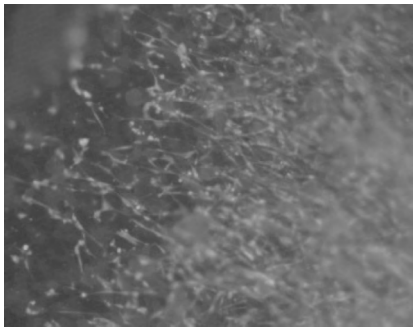
(a) Film without QDs



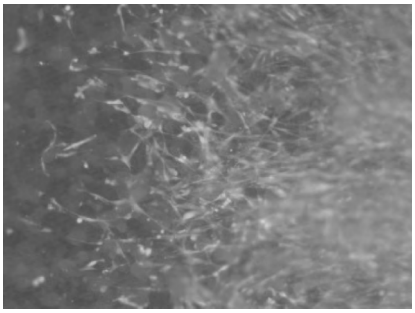
(b) Film doped 50 ℃ QDs



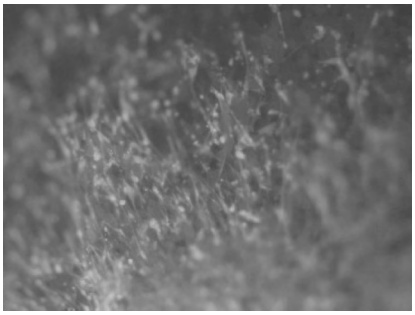
(c) Film doped 70 ℃ QDs



(d) Film doped 140 ℃ QDs



(e) Film doped 170 ℃ QDs



(f) Film doped 200 ℃ QDs

Fig. 7 The real PL graphs of the cells cultured on the films without QDs (a) and doped with 50, 70, 140, 170, and 200 ℃, for 25 min QDs((b)-(f)) (λ_{ex} = 450 nm)

3 Conclusions

The eletrospun CdSe-QDs-doped porous films towards cancer therapy were synthesized. Glycerol make the synthesis of the QDs environmental friendly and the emissive CdSe QDs covers from 495 -595 nm of the emission region, with the highest QY of 78.28%. The cell proliferation assay shows the eletrospun CdSe-QDs-doped films have excellent cytocompatibility. Especially, when the electrospun films are doped by the QDs synthesized at 170 ℃ for 25 min, the cells grow the best. What's more, the eletrospun CdSe-QDs-doped porous films preserve the original QDs' fluorescence in the region from 510 to 580 nm. Furthermore, the porous structure of this film is predicted to load drugs in the cancer therapy. Finally, the cell live-dead staining graphs show both the green cell and the as-sythesized films.

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