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Flexible luminescent CdSe/bacterial cellulose nanocomoposite membranes

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ABSTRACT

Flexible luminescent membranes based on bacterial cellulose (BC) were successfully fabricated by the in situ synthesis of the CdSe nanoparticles on the BC nanofibers. X-ray diffraction (XRD) patterns and field emission scanning electron microscopy (FE-SEM) revealed that CdSe nanoparticles were homogeneously dispersed on the BC nanofibers. The thermal stability of BC was greatly increased with the inclusion of CdSe nanoparticles. The CdSe/BC nanocomposite exhibited good photoluminescence properties and excellent mechanical properties. This work provides an effective method for the construction of flexible BC membranes with photoluminescence properties, which are promising for applications in the fields of security papers, sensors and flexible luminescent membranes.

1. Introduction

CdSe quantum dots (QDs) have attracted enormous interest in the past several years due to their unique optical properties such as high photostability, broad absorption, narrow and symmetric emission spectra, size tunable optical emission, longer fluorescence lifetime than organic fluorophores and negligible photobleaching (Michalet et al., 2001; Rosenthal, McBride, Pennycook, & Feldman, 2007). They have been used in many different applications including sensors (Shang, Wang, & Jin, 2009), non-linear optical devices (Gerdova & Hache, 2005) and solar cells (Chen et al., 2009). However, the applications of QDs in the fields of biodiagnostics, bioanalytics, photonics and optoelectronics require combination of the QDs with polymers (Chang, Peng, Zhang, & Pang, 2009). Several research works about the preparation and the properties of QD/cellulose and QD/cellulose derivatives nanocomposites have been reported for their potential applications in security paper or sheets with optical signatures (Abitbol & Gray, 2009; Abitbol, Wilson, & Gray, 2011; Generalova et al., 2009; Luna-Martinez et al., 2011; Niu, Gu, & Huang, 2011). However, natural fibers are composed of only 55–65% cellulose where the isolation and purification of fibers are needed. Besides, the current environmental issues show a pressing need for innovative, sustainable, and recyclable materials with performance at the same level or better than conventional natural fibers (Hu, Chen, Yang, Liu, & Wang, 2011).

Unlike native cellulose obtained from other sources, i.e., land plants or algae, bacterial cellulose does not contain collateral biogenic compounds like lignin, pectin and hemicellulose requiring purification and can therefore be separated in its purest form during the extracellular synthesis process (Gelin et al., 2007). In addition, BC presents unique properties and structures such as high crystallinity, good biocompatibility, ultra fine three dimensional (3D) network with a distinct tunnel and pore structure, high specific surface area with a great deal of hydroxyl groups and excellent mechanical strength (Li et al., 2009; Zhang et al., 2011). These characteristics make BC a good template or matrix for the synthesis of nanoparticles and nanowires (Hu et al., 2009; Hu, Chen, Zhou, & Wang, 2010; Yang et al., 2011).

In this paper, CdSe/BC nanocomposite has been successfully fabricated by in situ method using BC as matrix. To our best knowledge, this is the first report on incorporation of CdSe nanoparticles into bacterial cellulose. The resultant CdSe/BC nanocomposite were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), field emission scanning electron microscopy (FE-SEM), thermogravimetric analysis (TGA), and mechanical measurements. Besides, the optical properties of the nanocomposite membranes were studied by ultraviolet–visible (UV–vis) and photoluminescence (PL) spectra.

2. Experimental

2.1. Materials

BC membranes were kindly provided by Hainan Yeguo Foods Co. Ltd with the degree of polymerization (DP) of 1020. The DP of BC

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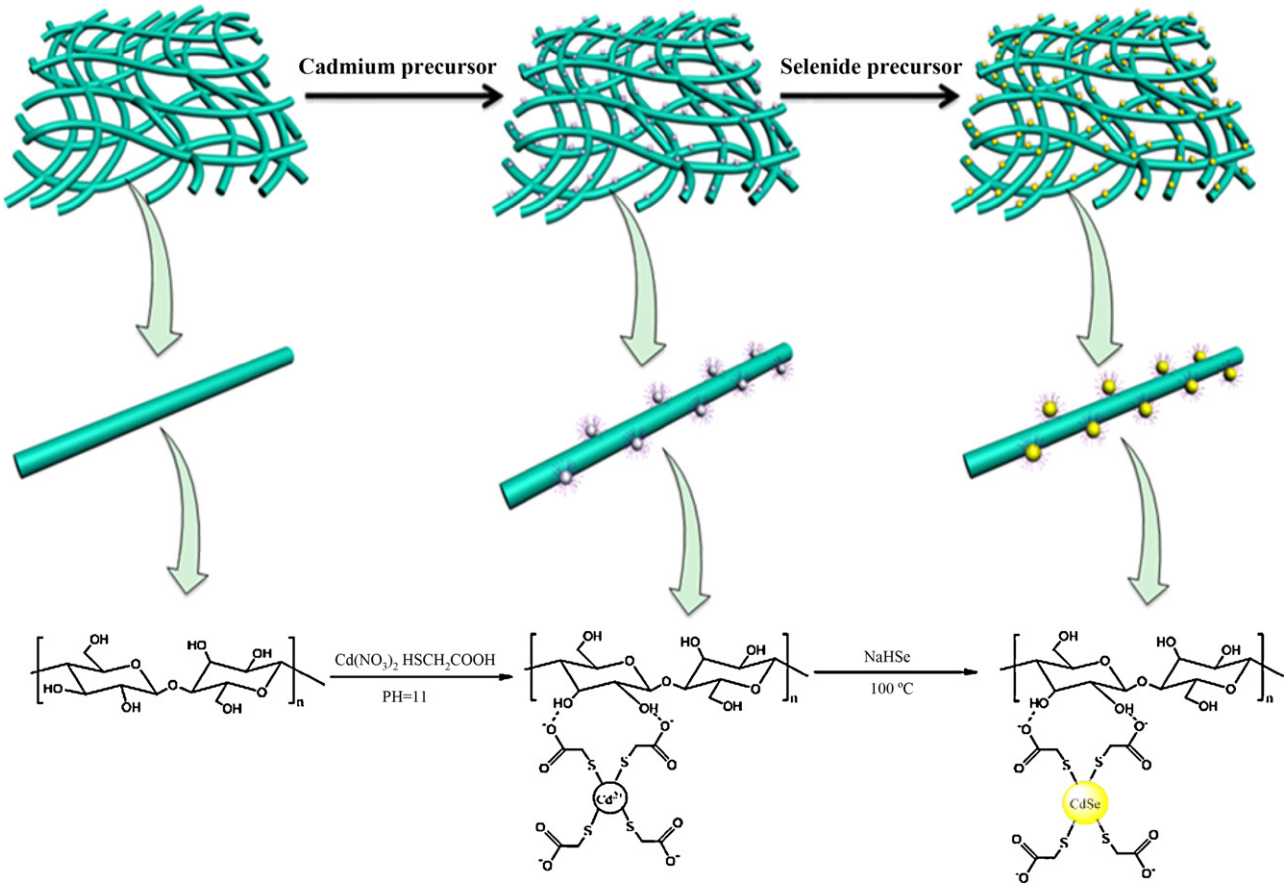

Fig. 1. Schematic diagram of the formation of CdSe/BC nanocomposite.

was determined viscometrically using copper (II)-ethylenediamine (Cuen) as solvent at 25 °C (Lu & Shen, 2011). Thioglycolic acid was purchased from Aladdin Reagent Co. Ltd. The other chemicals were purchased from Sinopharm Chemical Reagent Co. Ltd. All chemicals were used as received without any further treatment. High purity water with resistivity of 18.2 MΩ cm was used in the whole experimental process.

2.2. Preparation of precursor solutions

2.2.1. Preparation of cadmium precursor

0.16 mmol $Cd(NO_3)_2{\cdot}4H_2O$ was dissolved in 20 mL of pure water in a beaker with magnetic stirring and then 0.4 mmol of thioglycolic acid was added. The pH value of the resultant solution was adjusted to 11 with 2 wt% NaOH solution. This cadmium precursor solution was coded as "SOL-A".

2.2.2. Preparation of selenide precursor

Sodium hydrogen selenide (NaHSe) solution was prepared by stirring the aqueous solution containing 4 mmol/L elemental Se and 24 mmol/L $NaBH_4$ for 1 h under N_2 atmosphere. This selenide precursor solution was coded as "SOL-B".

2.3. Fabrication of CdSe/BC nanocomposite

The BC membranes (3 cm × 4 cm × 0.5 cm) were treated with 1 wt% NaOH solution for 12 h and then were washed with pure water sufficiently until the filtrate became neutral. The purified BC membranes were immersed into a three-necked flask with a magnetic stirring bar containing 20 mL of the SOL-A for 24 h. Under the protection of nitrogen, 20 mL of SOL-B was injected into the three-necked flask and then the mixture was stirred for 1 h at 100 °C. Finally, the membranes were rinsed with pure water for several times and freeze-dried.

2.4. Characterization

The infrared spectra of BC and CdSe/BC nanocomposite membranes were recorded on a Nicolet NEXUS-670 FTIR. Each sample was grounded with dried potassium bromide (KBr) powder and compressed into a disc, and then was subjected to analysis. XRD patterns were obtained in a Rigaku D/max-2000 X-ray diffractometer with the Cu Ka radiation at a scanning rate of 2°/s ranging from 10° to 70° (2θ angle). The morphologies of the samples were characterized using S-4800 FE-SEM. Prior to analysis, the samples were cut into small pieces from the freeze-dried samples, and coated with a thin layer of evaporated gold. Thermal gravimetric was performed under nitrogen atmosphere using a Netzsch TG 209 F1 with a heating rate of 20 °C/min. Photoluminescence spectra were measured on a JASCO FP-6600 spectrofluorometer. UV–vis spectra were recorded with a Perkin–Elmer Lambda 35 UV–vis spectrophotometer in the transmission mode. Fluorescence micrographs were obtained by Olympus BX51 fluorescence microscope. The samples were excited by ultraviolet light (330–385 nm). Tensile strengths of the samples were measured using a WDW 3020 Universal Testing Machine at room temperature and a crosshead speed of 5 mm/min. Samples with 60 mm in length, 10 mm in width and 0.1 mm in thickness were used in the measurements.

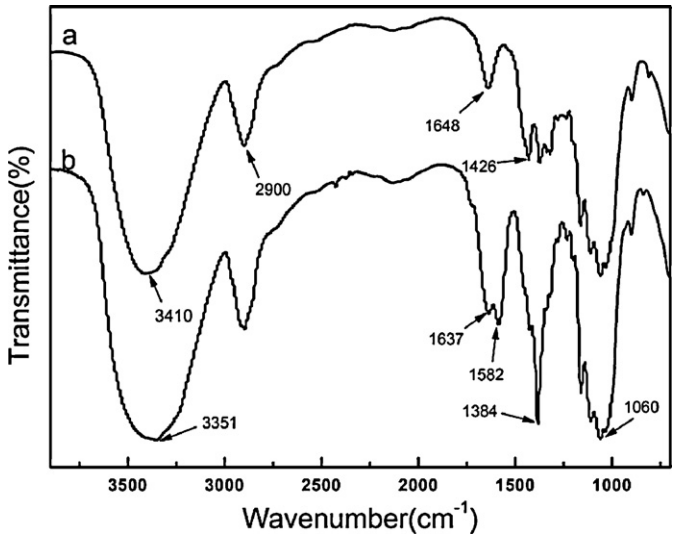

Fig. 2. The FTIR spectra of (a) pure BC and (b) CdSe/BC nanocomposite.

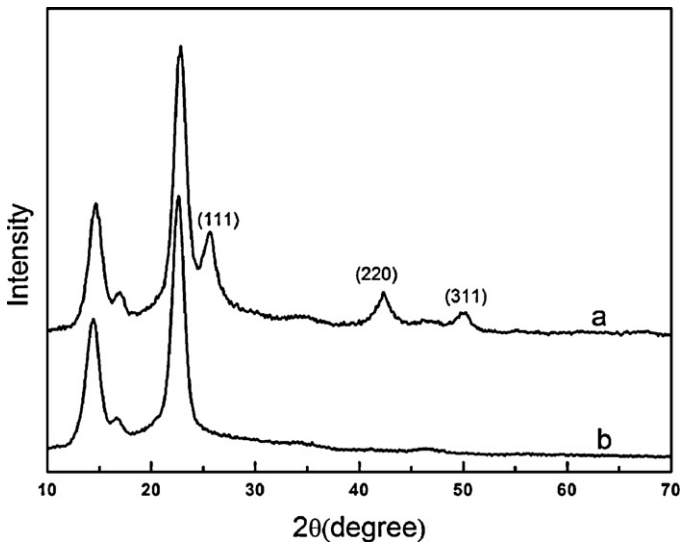

Fig. 4. XRD patterns of (a) CdSe/BC nanocomposite and (b) pure BC.

3. Results and discussion

3.1. Synthesis of CdSe/BC nanocomposite

The porous structure of BC membrane makes it easy for thioglycolic acid capped Cd^{2+} to penetrate into its inner space. Cd^{2+} ions are firstly anchored onto some BC nanofibers through the hydrogen bonds between the carboxylate anion of thioglycolic acid and the hydroxyl groups of BC (Martinez-Manez & Sancenon, 2006) during the soaking of BC in the cadmium precursor solution. When the selenide precursor solution is added, CdSe are formed almost immediately with the strong interaction between Cd^{2+} and Se^{2-}, as illustrated in Fig. 1. The interaction between BC and thioglycolic acid capped CdSe avoids the agglomeration of CdSe nanoparticles and assures the uniform distribution of CdSe nanoparticles on the surface of BC nanofibers.

3.2. FTIR spectroscopy

The FTIR spectra of BC and CdSe/BC nanocomposite samples are shown in Fig. 2. The bands at 3410, 2900, 1648 and 1060 cm^{-1} in Fig. 2a are associated with native BC (Hu, Chen, et al., 2011; Hu, Liu, Chen, & Wang, 2011). The strong band at 3410 cm^{-1} arises from the stretching of hydroxyl groups. The bands at 2900 and 1648 cm^{-1} originate from the C—H stretching and the H–O–H bending of the absorbed water. A strong band at 1060 cm^{-1} is due to the C–O–C pyranose ring skeletal vibration. Fig. 2b shows the spectra of the CdSe/BC nanocomposite. Compared with the spectra of pure BC, it can be seen that the absorption peaks at 3410 cm^{-1} and 1648 cm^{-1} in the spectrum of BC are shifted to 3351 cm^{-1} and 1637 cm^{-1} in the spectrum of the CdSe/BC nanocomposite, respectively. This phenomenon indicated that there is a strong interaction between the hydroxyl groups of the BC and the thioglycolic acid capped CdSe (Li et al., 2009). The absorption peaks at 1582 cm^{-1} and 1384 cm^{-1} can be assigned to the asymmetric and the symmetric vibration of carboxylate anion in thioglycolic acid (Jiang & Ju, 2007), respectively. The absence of the S—H stretching mode around 2560 cm^{-1} in the spectra clearly indicates that the thiol group of thioglycolic acid is bound to surface atoms of quantum dots through the Cd–S bond (Kalasad, Rabinal, & Mulimani, 2009).

3.3. FE-SEM and XRD analysis

The morphology of pure BC and the CdSe/BC nanocomposite was studied using FE-SEM and the images are shown in Fig. 3. From Fig. 3a, we can see the 3D porous network structure of BC that consists of continuous nanofibers with a diameter in the range from to 70 nm. This exquisite structure gives a good tunnel for Cd^{2+} adsorption and results in homogeneous distribution of Cd^{2+} on BC nanofibers (Li et al., 2009). Fig. 3b shows the FE-SEM image of CdSe/BC nanocomposite. It can be seen that the CdSe nanoparticles were formed in situ on the BC nanofibers and the nanoparticles with

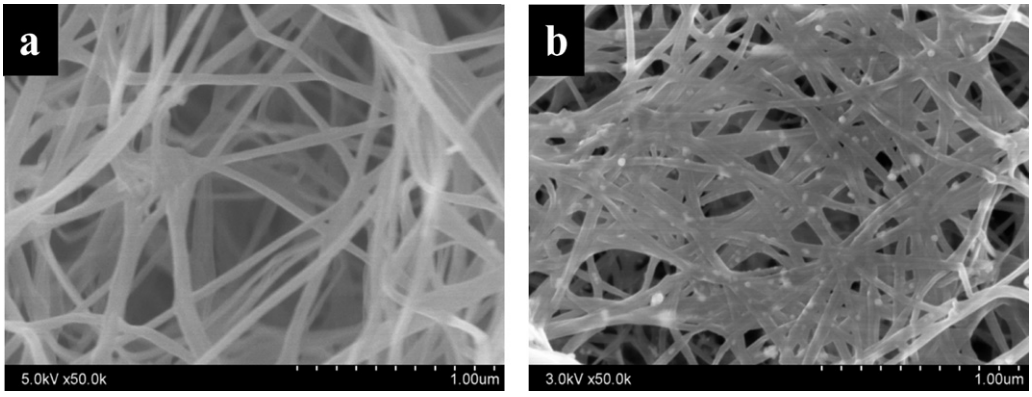

Fig. 3. FE-SEM images of (a) pure BC and (b) CdSe/BC nanocomposite.

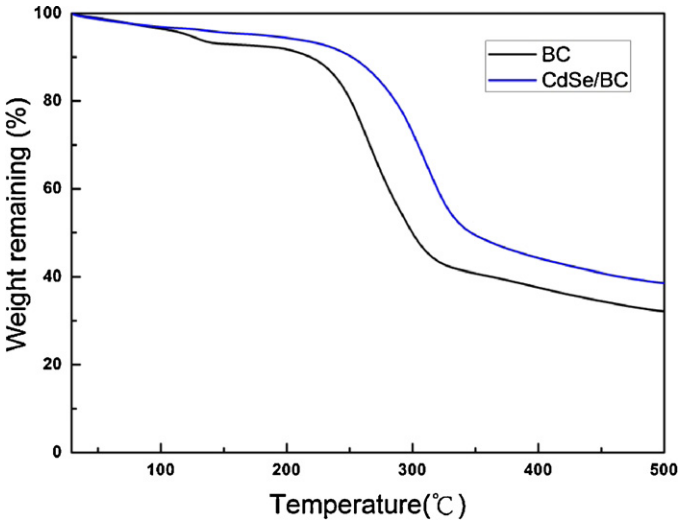

Fig. 5. TG curves of pure BC and CdSe/BC nanocomposite.

a size of about 20 nm were homogeneously dispersed on the fibers. The crystallographic nature of the nanoparticles in BC was further investigated by XRD to confirm the formation of CdSe nanoparticles. Compared with the XRD of pure BC sample (Fig. 4b), the broad diffraction peaks at 14.54°, 16.67° and 22.65° in the CdSe/BC nanocomposite shown in Fig. 4a are assigned to the crystallographic plane of (1 0), (1 1 0) and (2 0 0) reflection of BC (Tokoh, Takabe, Fujita, & Saiki, 1998). Another characteristic three major peaks at 25.70°, 42.32° and 50.25° correspond to the (1 1 1), (2 2 0) and (3 1 1) crystal planes of CdSe (Wang, Lu, & Tong, 2010). The results indicated that CdSe nanoparticles were successfully formed in BC matrix and the CdSe prefers cubic zinc-blended structure.

3.4. Thermal properties

The thermal stability of CdSe/BC nanocomposite was investigated with TG. Fig. 5 shows the TG curves of pure BC and CdSe/BC nanocomposite. As shown in the TG curve of pure BC, there are two significant weight loss platforms from ambient to 250 °C and 250–350 °C. The first weight loss platform is caused by the vaporization of the moisture present in the BC. The sharp weight loss in the second platform can be attributed to the destruction of the crystalline region of BC and decomposition of amorphous BC into monomer of D-glucopyranose and further into free radical (Hu, Chen, et al., 2011; Hu, Liu, et al., 2011). From the TG curve of CdSe/BC nanocomposite, we can find that it also experiences a similar weight loss process. Nevertheless, the onset degradation temperature of CdSe/BC nanocomposite is 38 °C higher than that of pure BC. In this sense, the thermal stability of CdSe/BC nanocomposite is higher than that of pure BC. This result also indicates the interaction between BC and CdSe nanoparticles.

3.5. Optical properties

Fig. 6 shows the UV–vis absorption spectra of CdSe/BC nanocomposite and pure BC and the PL spectra of CdSe/BC nanocomposite and pure BC. As seen in Fig. 6a, pure BC nearly exhibited no absorption in the selected region. In contrast, a significant absorption at about 445 nm can be observed in the UV–vis absorption spectrum of CdSe/BC nanocomposite. This absorption edge blue shifted 271 nm compared with the bulk CdSe, which indicates the quantum confinement effect of CdSe nanoparticles (Ma et al., 2002). The PL spectra of CdSe/BC nanocomposite and pure BC at room temperature with an excitation wavelength at 370 nm are shown

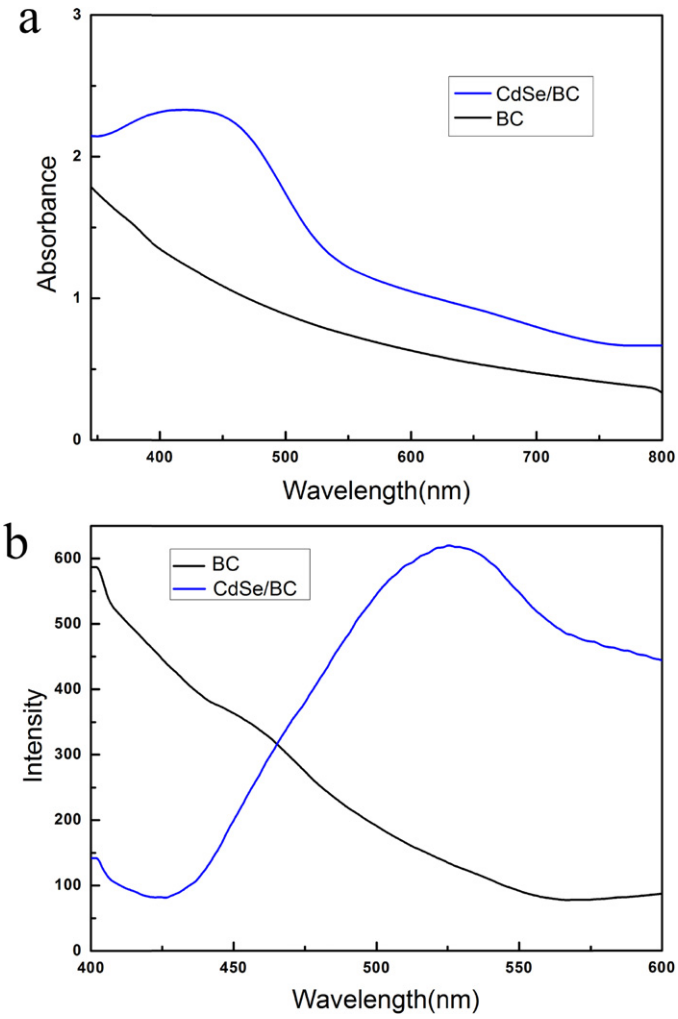

Fig. 6. (a) UV–vis absorption spectra of CdSe/BC nanocomposite and pure BC and (b) PL spectra of CdSe/BC nanocomposite and pure BC.

in Fig. 6b. Compared with the pure BC, CdSe/BC nanocomposite exhibits a significant emission peak at 529 nm, which is the typical luminescence of CdSe nanoparticles resulting from the transition of electrons from shallow states near the conduction band to selenium vacancies present near the valence band (Kang, Chang, Dai, & Chen, 2008).

Fig. 7 shows bright field micrograph of the CdSe/BC nanocomposite and the corresponding fluorescence micrograph taken by excitation with ultraviolet light (330–385 nm). The CdSe/BC nanocomposite membrane without excitation displays just like ordinary paper (Fig. 7a). In contrast, strong and well-defined green photoluminescence is clearly observed from the CdSe/BC nanocomposite membrane with excitation (Fig. 7b), indicating the nanocomposite membrane is endowed with luminescence property. The strong green photoluminescence can still be observed from the nanocomposite membrane after storage in ambient air for three months, which suggests the good stability of the CdSe/BC nanocomposite membrane.

3.6. Mechanical properties

The mechanical properties of CdSe/BC nanocomposite membranes were investigated by the tensile test. Fig. 8a shows the tensile behaviors of pure BC and CdSe/BC nanocomposite membranes. The tensile strength (31.9 MPa) and Young's modulus (325.9 MPa) of CdSe/BC nanocomposite membranes are lower than

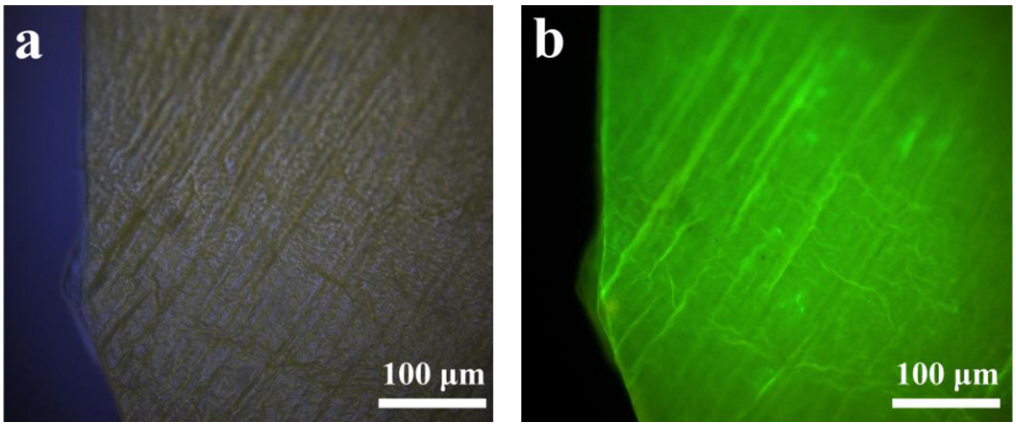

Fig. 7. Micrographs of the CdSe/BC nanocomposite membrane without excitation (a) and with excitation (b).

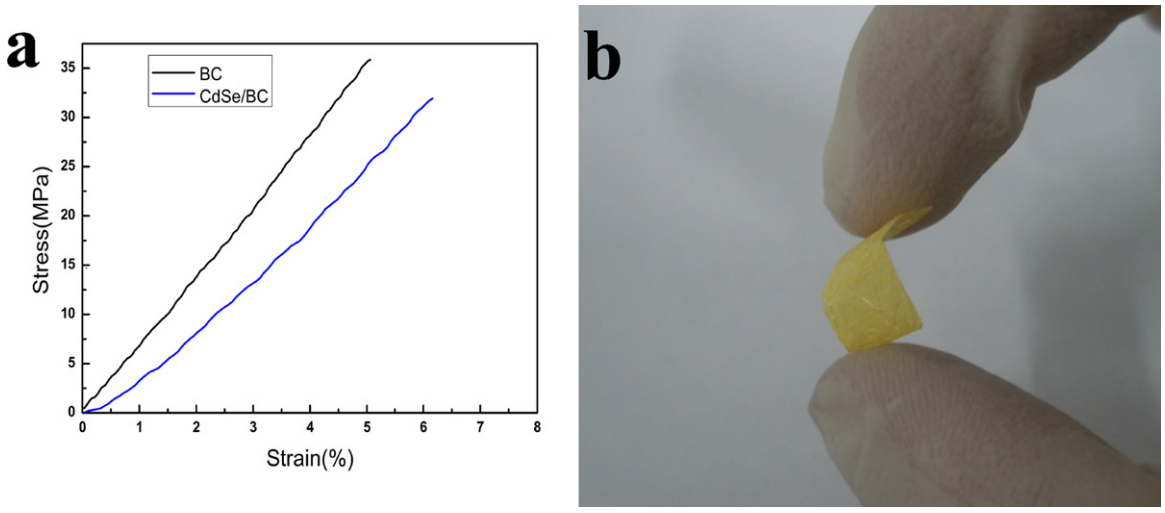

Fig. 8. (a) Tensile stress–strain behaviors of pure BC and CdSe/BC nanocomposite membrane, (b) photograph of the CdSe/BC nanocomposite membrane.

the tensile strength (35.9 MPa) and Young' modulus (681.7 MPa) of pure BC membrane. This decreased behavior of CdSe/BC membrane might be related with the reduction in crystallinity of BC caused by NaOH when being prepared in an alkaline environment. However, compared with the pure BC membrane, the elongation at break of CdSe/BC nanocomposite membrane is increased from 5.0% to 6.2%, indicting its striking flexibility. The nanocomposite membrane can be bended freely for many times without appearing apparent damage (Fig. 8b). In summary, the nanocomposite combines the excellent mechanical properties of BC membrane and the photoluminescence properties of CdSe quantum dots, which makes it a promising material in the applications of security paper, flexible luminescent membranes and sensors.

4. Conclusion

The novel CdSe/BC nanocomposite membranes were successfully synthesized in situ using BC as the matrix. It is found that the CdSe nanoparticles with a size of about 20 nm were homogeneously dispersed on the BC nanofibers, which greatly improves the thermal stability of BC. The result from the FTIR spectra shows that there is a strong interaction between the hydroxyl groups of the BC and the thioglycolic acid capped CdSe. The nanocomposite integrates the photoluminescence properties of CdSe quantum dots and the good mechanical properties of BC membrane. Further investigation such as the influence of different concentration of reaction solution and reaction time on the properties of the nanocomposites is in progress.

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