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Biocompatible and Photoluminescent Keratin/Poly(vinyl alcohol)/Carbon Quantum Dot Nanofiber: A Novel Multipurpose Electrospun Mat

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Abstract: Carbon quantum dots (C-dots) triggered photoluminescent keratin/poly(vinyl alcohol) (PVA)/C-dots nanofibers (NFs) with optical transparency and biocompatibility were prepared by an electrospinning process. The synthesized NFs were characterized by field-emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FTIR), ultraviolet-visible spectroscopy, and spectrofluorometer. C-dots are capable of emitting excitation dependent photoluminescence (PL) emission spectra at room temperature and are nontoxic at reasonably high concentrations. Optically transparent keratin/PVA/C-dots NFs were found to exhibit excitation dependent PL emission at the wavelengths of 488, 535, and 625 nm during excitation at the wavelengths of 360, 480, and 545 nm, respectively, similar to the C-dots. *In vitro* cytotoxicity tests against NIH-3T3 cell lines revealed a good biocompatible nature of keratin/PVA/C-dots. The results indicated that the fabricated composite NFs mat not only exhibited a well preserved quantum confinement effect of the C-dots along with its transparency but also showed biocompatibility in the living cell environment.

Keywords: electrospinning, carbon quantum dots, keratin, poly(vinyl alcohol), photoluminescence, biocompatibility.

Introduction

Electrospinning technique has been extensively used by the scientific community for fabricating continuous fibers from polymers,[1,2] ceramics,[3] and hybrid (organic/inorganic) compounds.[4] A large number of natural and synthetic polymers have been electrospun into nanofibers for specific application in various fields, including waste-water treatment, air purification, opto-electronic devices, and biomedical science such as wound dressing, tissue engineering, cell culture, *etc*.[5-7] Recently, the exploration of electrospun biopolymers such as keratin, silk fibroin, chitosan, and gelatin has been paid huge attentions due to their biocompatibility and environment friendly nature.[8-10] Development of optically transparent and photoluminescent nanofibers (PL NFs), specially derived from biopolymers has attracted more interest because of their low thermal expansion and continuous roll to roll processing capability to future electronic devices like flexible display, solar cells, e-paper, and flexible circuit technology.[11,12]

Carbon quantum dots (C-dots), a new member of the nanocarbon family, have drawn attention due to their unique properties, such as robustness, chemical inertness, and superior stability against photobleaching, biocompatibility, and low cytotoxicity.[13,14] Recently, our research group has employed electrospinning process as a strategy to incorporate the insoluble particles inside the nanofibers. Unique mechanical, electrical, chemical, and optical properties have been achieved by decorating electrospun nanofibers with C-dots.[15,16] A variety of quantum dots, including C-dots have been reported in the literature to be successfully incorporated into polymer NFs to employ versatile application due to their excellent photoluminescence (PL) properties, the small size of single quantum dots, good dispersibility in the polymer environment.[16-19]

C-dots have been demonstrated as effective nanofillers in polymers to design composite sub wavelength optical waveguides and efficient photoconductive devices at infrared length.[20] The carbon quantum dots embedded electrospun nanofibers can also be applied in sensing and cell imaging.[21] However, there are very few reports until now on the fabrication of fluorescent composite nanofibers. In this study, we have presented the electrospun keratin/poly(vinyl alcohol) (PVA)/carbon quantum dots (C-dots) NFs mat with PL properties as well as biocompatibility. It is already reported that C-dots have been used to

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fabricate excellent opto-electronic devices, antibacterial agents, and fluorescence bio-imaging probes, transparent NFs or security-check devices.[22-24] Our group has already developed optically transparent and flexible keratin/PVA mat *via* electrospinning process.[25] Therefore, to exploit the optically transparent and flexible properties of keratin/PVA nanofiber mat and photoluminescent properties of C-dots, here, we have successfully reported the fabrication of C-dots incorporated keratin/PVA nanocomposite mats by the electrospinning process followed by simple water treatment. The incorporation of C-dots in the composite nanofiber mat has not only introduced the PL properties to keratin/PVA/C-dots NFs but also maintained good biocompatibility in living cell environments which lead to the multifaceted utilization of the hybrid nanofiber mat.

Experimental

Materials. Poly(vinyl alcohol) (PVA, with weight averaged molecular weight M_w=85,000-124,000 g/mol, 87-89% hydrolyzed), glyoxal (40 wt% in H_2O), *N*,*N*-dimethylformamide (DMF, 99.9%), sodium disulfite ($Na_2S_2O_5$), sodium dodecyl sulphate (SDS), urea (99.9%), citric acid (99.5%), and ethanol (99.9%) were purchased from Sigma-Aldrich. Human hairs were obtained from the local barber (Jeonju, South Korea). All the chemicals were used as received. Double-distilled water was used as a solvent throughout the experiment.

Synthesis of Carbon Dots (C-dots). Microwave assisted pyrolysis method was employed for the synthesis of C-dots according to our previous report with some modification.[16] In brief, 1g of citric acid (CA) and 1 g of urea were dissolved in 10 mL of distilled water and kept under microwave (700W) treatment for 5 min. The resulted brown solid was dissolved in water and centrifuged at 12,000 rpm for 15 min to remove the large or agglomerated particles. The top part was descended and the remaining solution was kept overnight in an oven at 80 ºC. Finally, the black dried sample was collected, measured, and dispersed in water again. The brownish solution having concentration of 50 mg/mL was used for further experimentation. The as derived C-dots were characterized by transmission electron microscopic (TEM) images and (PL) spectra. The observed information was identical with the reported results.[26]

Quantum Yield. Quinine sulfate was used as standard reference material for determination of quantum yield (QY) of C-dots in solution. The QY of quinine sulfate is reported to be 54% in the literature when dissolved in 0.1 M H_2SO_4. The quantum yield of as synthesized C-dots in dimethyl sulfoxide (DMSO) was calculated as according to our previous publication[16] by applying the following equation:

$$\varphi_x = \varphi_{std}[I_x/A_x][A_{std}/I_{std}][\eta_x/\eta_{std}]^2$$

where φ is the quantum yield, "*std*" refers the standard reference, I is the measured integrated emission intensity, η is the refractive index, and A is the optical density. The quantum yield of the as obtained C-dots is about 23%, comparable to the previously reported value.

Preparation of the Keratin/PVA/C-Dots Blend Solution. Sulphitolysis process was carried out to extract keratin from human hair in accordance with our previous report.[25] In brief, certain amount of human hairs was cleaned with water containing 0.5% SDS and washed with distilled water to remove the fatty matter present. The washed hairs were conditioned at 50 ºC for 24 h maintaining 65% relative humidity. 2.5 g of conditioned hairs were cut into snippets of a few millimeters and added to the 250 mL (8 M) aqueous solution of urea containing 2.5 g of $Na_2S_2O_5$ and 1.25 g of SDS. The mixture was heated to 100 ºC, shaken for 1 h and then cooled at room temperature. Next, the solution was dialyzed against 500 mL of water containing 0.1 wt% $Na_2S_2O_5$, using a cellulose tube (molecular-weight cutoff 12-14 kDa) for 3 days. The keratin/PVA blend solution was prepared by adding PVA directly into the keratin aqueous solution in order to obtain 10 wt% of total polymeric concentration. The glyoxal solution (10 wt% with total polymer) was then added into the polymeric solution as a cross-linking agent. The pH of the system was adjusted at 2.0-3.0 by adding phosphoric acid. Keratin/PVA/C-dots blend solutions containing 0.05, 0.5, and 1.0 wt% of C-dots were prepared by adding the required amount of C-dots and stirred for 6 h at room temperature.

Fabrication of Transparent Keratin/PVA/C-Dots Nanofiber Mat. Electrospinning was carried out at room temperature to fabricate the keratin/PVA/C-dots nanofibers by applying 15 kV applied voltage and tip-to-collector distance of 15 cm. As-spun keratin/PVA/C-dots blend NFs were collected on Teflon paper and dried at 50 ºC under vacuumed condition for 24 h and then cured at 120 ºC for 10 min. For comparison, keratin/PVA nanofiber mat was also prepared by the aforementioned procedure without using C-dots.

A very simple technique was carried out to obtain transparent nanofiber mat without any additive in which the as prepared keratin/PVA/C-dots nanofiber mat was immersed in water for 10 min and oven dried at 50 ºC. Optically transparent nanofiber mat was obtained after the completely drying.

Cell Culture and Biocompatibility Test. NIH-3T3 cell lines were cultured in Defined K-SFM serum free medium containing 10% fetal bovine serum (FBS), penicillin (100 IU/mL) and streptomycin (100 μg/mL). The cell suspension was kept in the incubator (Thermo Electron Corporation, USA) at 37 ºC, 5% CO_2; and 95% humidity. The cytotoxicity and biocompatibility of C-dots was evaluated by the 3-[4,5-dimethylthiazol-2-yl]-2,5-diphenyltetrazolium bromide (MTT) assays. Briefly, electrospun keratin/PVA and keratin/PVA/C-dots with same dimension were cut and sterilized under UV radiation for 1 h. The samples were washed three times with PBS prior to transfer to individual 96-well tissue culture plates. Cells were seeded onto the surface of a scaffold, and grown in the appropriate medium. The culture medium was removed and washed twice with sterile PBS followed by the addition of 20 μL of 0.5 mg/mL MTT solution to each well right after incubation at 37 ºC in a humidified

5% CO_2 incubator for different days. The incubation was continued for 1 h before the media was removed. DMSO (100 μL) was added to each well and mixed to ensure dissolving of the crystal formazan before the absorbance at 570 nm was measured. The viability experiments were done in triplicates and each data point represents the average of at least 3 independent experiments. The data were expressed as mean±standard deviation (S.D). The obtained data were analyzed using statistical analysis software (SAS). One way analysis of variance technique was applied to observe the significance between the groups.

Characterization. The surface morphology of the composite NFs mat was studied by field-emission scanning electron microscope (FE-SEM, S-7400, Hitachi, Japan). Fourier transform infrared (FT-IR) spectra were recorded using an ABB Bomen MB100 Spectrometer (Bomen, Canada). UV-Vis absorption and transmittance spectra were measured on a TU-1810 UV-Vis Spectrophotometer (Pgeneral, China). Photoluminescence (PL) emission measurements were performed using LS50B Luminescence Spectrometer (Edinburgh Instruments, UK). The X-ray photoelectron spectroscopy (XPS) measurements were performed on a Thermo Scientific K-Alpha KA1066 spectrometer using a monochromatic AlKα X-ray source ($h\upsilon$=1486.6 eV).

Results and Discussion

Surface Morphologies of Keratin/PVA/C-Dots Composite NFs. FE-SEM images of keratin/PVA/C-dots composite NFs containing 0.05, 0.5, and 1.0 wt% of C-dots were captured before and after immersion in water and compare with the keratin/PVA nanofibers mat (Figure 1). It was observed that the as-spun composite NFs exhibited randomly oriented bead free, smooth surface with almost uniform diameters along their length before immersion in water. Also, many large interstices were observed between the NFs. The diameter of NFs before immersing in water (Figure 1(b)-(d)), in comparison with C-dots free keratin/PVA (Figure 1(a)), found to be reduced noticeably after blending with different concentration of C-dots. The diameter of the C-dots free keratin/PVA NFs before immersion in water was observed to be within the range of 180-220 nm where as it was reduced to 100-150 nm in the case of keratin/PVA containing 1.0 wt% of C-dots. On the contrary, the NFs were found to be densely packed after immersion in water in the absence and the presence of C-dots, and the interstices between NFs were also reduced slightly as shown in Figure 1 ((a')-(d')). The relative diameter also found to be increased by several orders as NFs experienced swelling during the water treatment and the interfiber space was reduced due to their diameter expansion. This can be attributed to the hydrophilic character of the PVA which is the backbone of the composite NFs.[25] To clearly assess the incorporation of the C-dots on the surface of nanofiber, TEM images of the pristine C-dots and keratin/PVA/C-dots composite NFs were taken and presented in Figure 2. The size of the pristine C-dots was found to be in the range of 3-5 nm (Figure 2(a)). In the case of composite nanofiber containing different amount of C-dots, it can be seen that the C-dots are distributed throughout the surface of com-

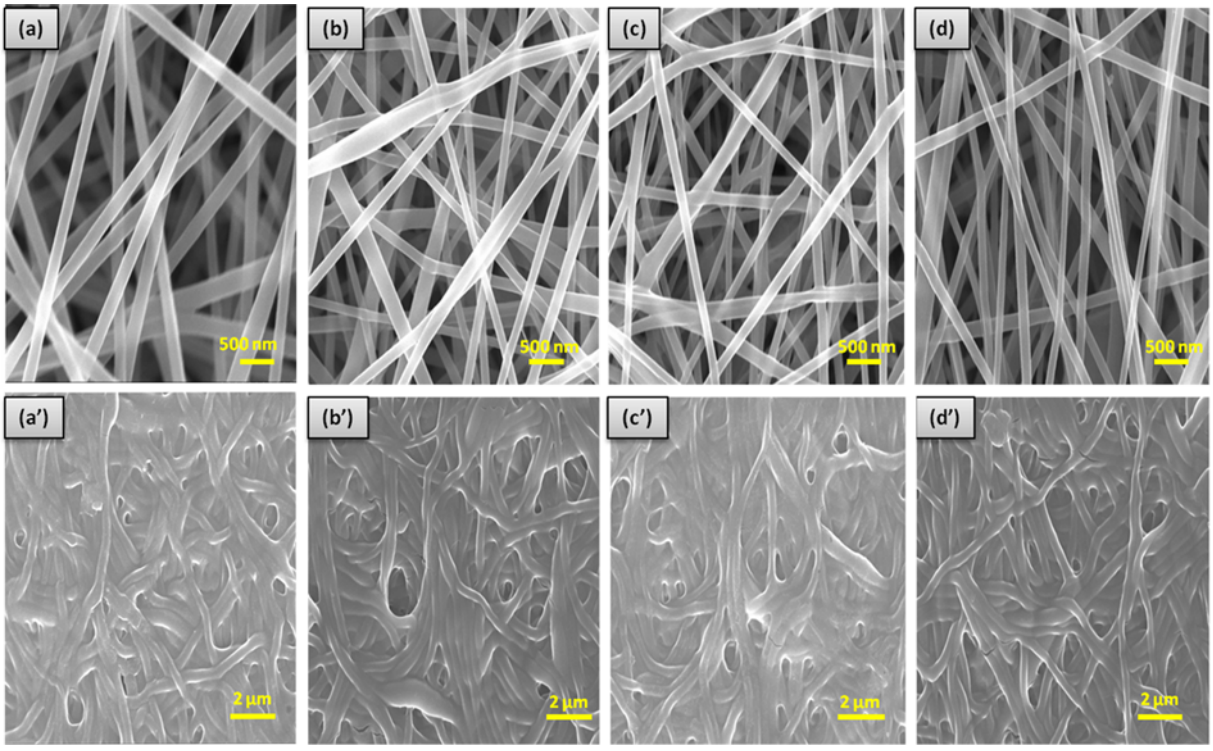

Figure 1. FE-SEM images of (a) keratin/PVA nanofiber, (b) keratin/PVA/C-dot (0.05 wt%), (c) keratin/PVA/C-dot (0.5 wt%), and (d) keratin/PVA/C-dot (1.0 wt%), respectively and (a')-(d') are their respective FE-SEM images after water treatment.

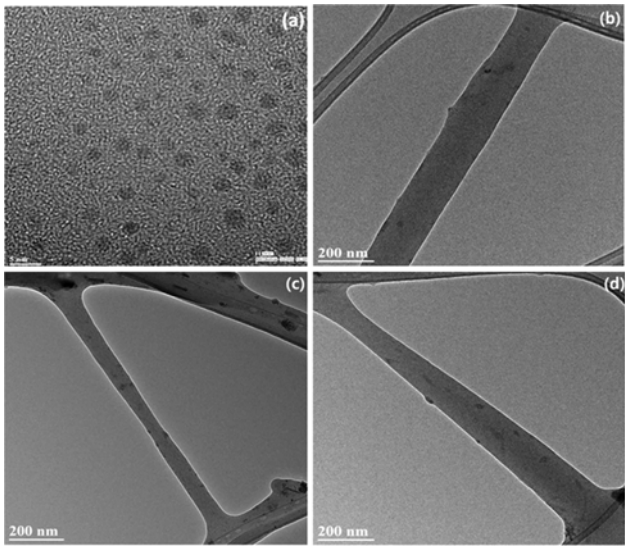

Figure 2. TEM images of (a) C-dots, (b) keratin/PVA/C-dot (0.05 wt%), (c) keratin/PVA/C-dot (0.5 wt%), and (d) keratin/PVA/C-dot (1.0 wt%).

posite nanofibers with some aggregations (Figure 2(b)-(d)).

FTIR Analysis. The FTIR spectra of C-dots and keratin/PVA nanofiber containing different amount of C-dots were recorded in order to study the surface functional groups of C-dots and their interaction with the polymer. The data are presented in Figure 3(a). As in the figure, the C-dots showed a broad absorption band at 3100-3500 cm^{-1} which is attributed to O-H and N-H group. Absorption bands at 1617-1770 cm^{-1} are assigned to C=O group which indicate the surface carboxylic group. The absorption band at 1570 cm^{-1} indicated the amide (CONH) bending.[16] The keratin/PVA NFs exhibited broad absorption peak at 3100-3600 cm^{-1} which can be attributed to the hydrogen bond between the -NH_2 groups of keratin and -OH group of PVA.[25] The absorption bands at about 1661, 1539, and 1246 cm^{-1} were the characteristic peaks of amide I, II, and III, respectively.[27] The absorption bands at 1734 cm^{-1} are assigned to stretching vibrations from C=O group present in the composite NFs.[16] In the keratin/PVA/C-dots composite NFs, it was observed that the addition of C-dots caused decrease in intensities of the absorption bands at 1661 cm^{-1} and broadening the peak with the increasing concentration of C-dots. Our previous report[15] demonstrated that C-dots have different functional groups in the form of -OH, COOH, CONH, *etc*. The presence of functionalities on the C-dots was helpful for the good dispersion in aqueous media. Therefore, after the electrospinning process, we obtained homogeneously distributed C-dots throughout the body of the nanofiber. The broadening of the peak of keratin/PVA in the presence of C-dots might be resulted from the further interaction and the formation of hydrogen bonding between surface functional groups of C-dots and available functional groups of keratin/PVA nanofiber. Further, X-ray photoelectron spectroscopy (XPS) measurements were carried out in the region from 0 to 950 eV to investigate the chemical composition of the nanofiber composites. In order to further confirm the successful incorporation of C-dots in the nanofiber mats the XPS spectra of keratin/PVA and keratin/PVA/C-dots (1.0 wt%) are compared. As shown in Figure 3(b), the full scan XPS spectrum of keratin/PVA reveals C 1s and O 1s peaks located at approximately 284.61 and 531.11 eV, respectively. In the case of keratin/PVA/C-dots (1.0 wt%), the existence of N 1s peak at 399.13 confirmed the presence of C-dots in the composite nanofibers.

Optical Transparency of Keratin/PVA/C-Dots Composite NFs. The focus was retaining the transparency of the fabricated keratin/PVA/C-dots NFs after incorporation of C-dots.

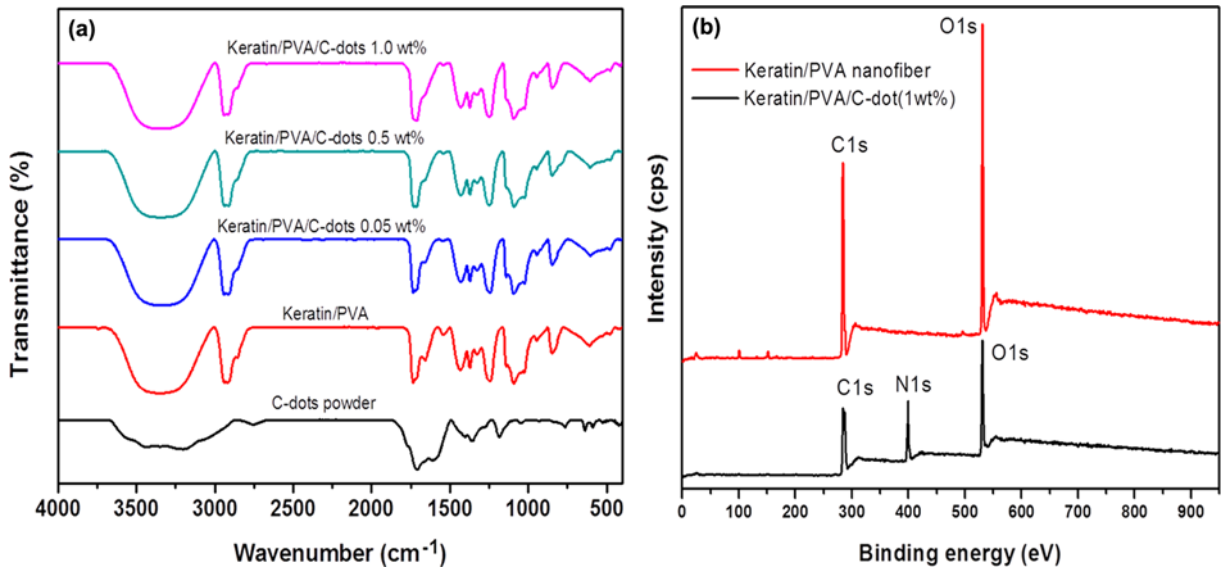

Figure 3. (a) FTIR spectra of different formulation of NFs mat after immersion in water (b) and the XPS survey of keratin/PVAC/C-dots (1.0 wt%) mat as compared to keratin/PVA nanofiber.

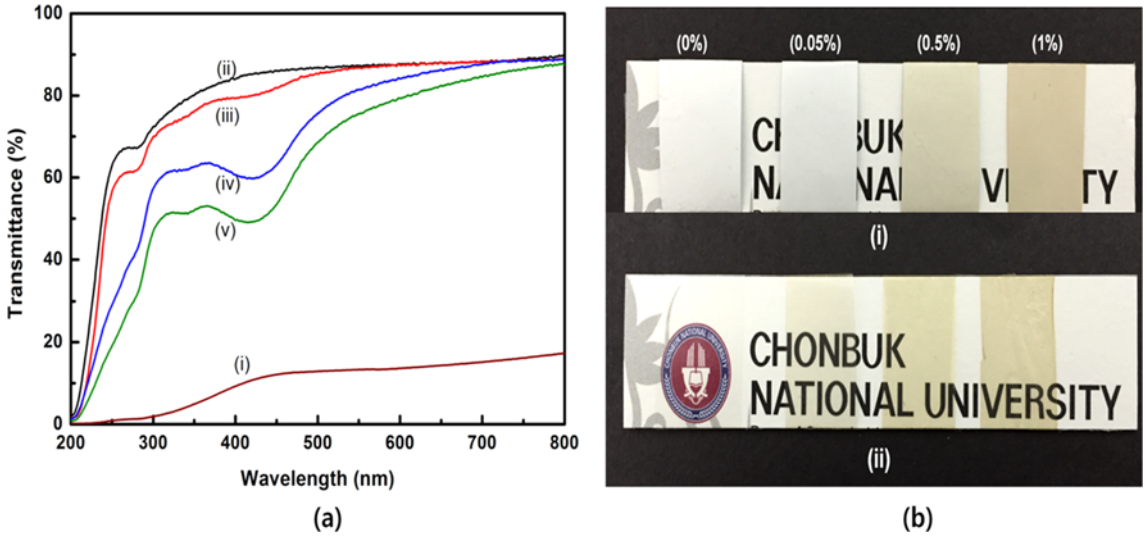

Figure 4. Transmittance spectra (a) of keratin/PVA nanofiber mat before (i) and after (ii) immersion in water. Transmittance spectra of ketatin/PVA/C-dots: 0.05 (iii), 0.5 (iv), and 1.0% (v), respectively. Visual image (b) of text under the NFs mat before (i) and after immersion (ii) in water.

Therefore, the light transmission spectra of keratin/PVA and keratin/PVA/C-dots NFs mat before and after immersion in water were recorded and illustrated in Figure 4. The keratin/PVA NFs mat found to exhibit negligible transmittance before immersion in water as shown in Figure 4(a)(i); however, tremendous transparency was recorded after immersion in water and the NFs mat offered high transmittance above 82% in the visible wavelength range as shown in Figure 4(a)(ii). The lack of transmittance in this mat before immersion in water seems to be caused by its high surface roughness due to the presence of large interstices between the NFs, which turned the surface of NFs mat bumpier and caused the scattering of light severely. After the water treatment, the NFs mat converted to densely packed NFs and interstices in between the NFs were small enough, which caused a drastic decrease in its surface roughness to avoid the light scattering thus making this composite material highly transparent. It was interesting to observe the transparency of the NFs mat even after blended with C-dots. As shown in Figure 4(a)(iii), the keratin/PVA NFs mat containing 0.05 wt% C-dots still exhibited light transparency over 78% in the visible range with little amount of absorption in the wavelength range of 400-450 nm. On the other hand, transmittance of light found to be decreased significantly at the wavelength of 400-450 nm to 60% and 50% for the mat containing 0.5 and 1.0 wt% C-dots respectively. However, in both cases the transmittance was found to be increased again over 80% in the visible wavelength as shown in Figure 4(a)(iv) and (v). The reason behind the significant reduction of transmittance of light of keratin/PVA NFs mat is the presence of C-dots within the fiber matrix. The interaction between the surface functional group of C-dots and the keratin/PVA fiber might be responsible for the absorption of some portion of visible light. The corresponding images of text under the fabricated keratin/PVA and keratin/PVA /C-dots NFs mat are depicted in Figure 4(b)(i) and (ii) before and after immersion in water respectively which clearly indicates their relative transparency.

Photoluminescence Properties of Keratin/PVA/C-Dots Composite NFs. C-dots are capable to demonstrate excitation dependent PL emissions at room temperature[16] As in the Figure 5(a), three emission spectra were observed in the wavelength of 483 (Figure 5(a)(i)), 532 (Figure 5(a)(ii)), and 615 (Figure 5(a)(iii)) nm from same sample solution when it was excited at the wavelength of 360, 480, and 545 nm, respectively. It was found that the C-dots, synthesized in this work, dominantly emitted at the wavelength of 483 nm and other emission spectra at 532 and 615 nm found to be less enhanced as compared to the first one. The obtained results showed that the PL behavior of the C-dots is excited-dependant. These phenomena of the emission property may originate from the size of the C-dots, the availability of sp2 sites, aromatic conjugated structure, and the defects in the structure. It has been already reported that the presence of different sizes and multiple surface emissive trap status may lead to inter-system crossing and adjacent vibrational relaxation of excited electrons, thereby triggering PL emission with the corresponding energy. Therefore, polymer NFs blended with C-dots are also expected to exhibit the same characteristic PL performance. The PL emission spectra of keratin/PVA/C-dots NFs mats were studied and are presented in Figure 5(b). As shown in Figure 5(b), no observable excitation dependent emission within visible spectrum range was found from C-dots free keratin/PVA mat when it was excited at the wavelength of 360, 480, or 545 nm. However, keratin/PVA/C-dots NFs mat blended with different amount of C-dots emitted excitation dependent emission spectra at the wavelength of 488, 535, and 625 nm during excitation at the wavelength of 360, 480, and 545 nm, respec-

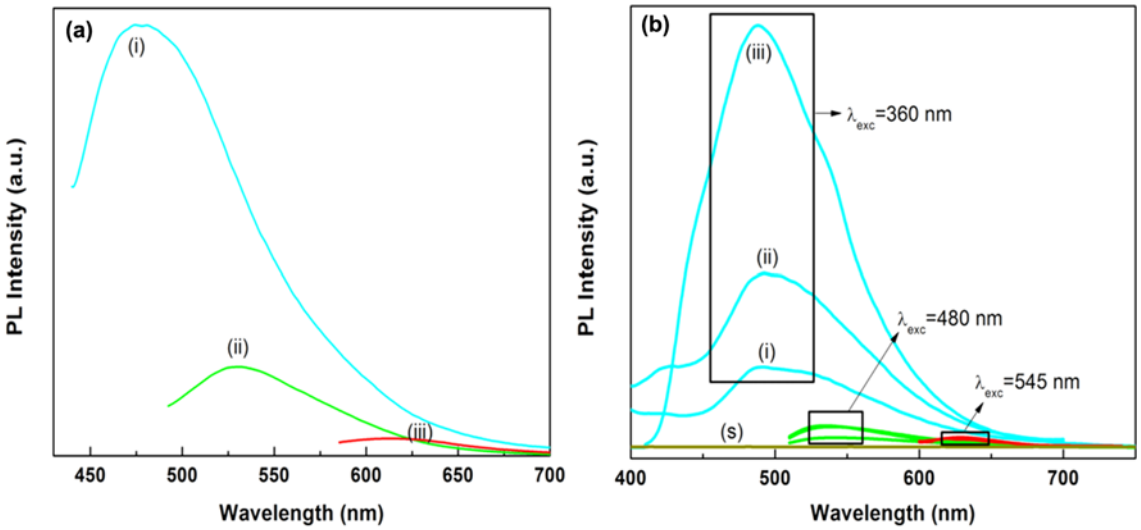

Figure 5. PL emission spectra of (a) C-dots and (b) keratin/PVA/C-dot with 0.05 wt% (i), 0.5 wt% (ii), and 1.0 wt% (iii), respectively.

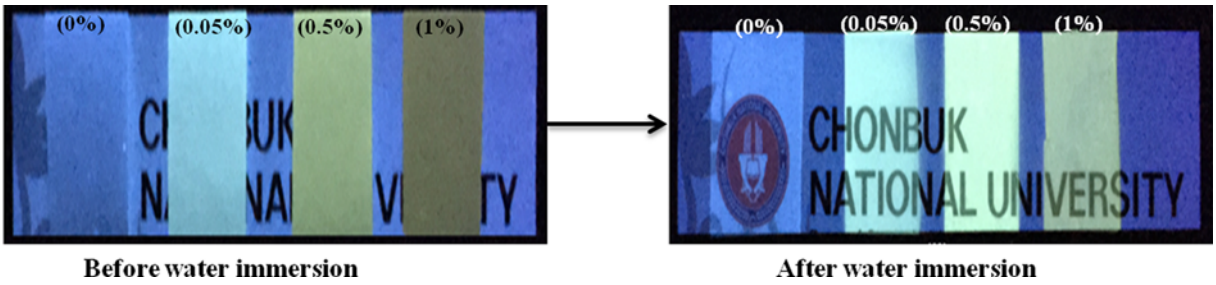

Figure 6. NF mat before and after immersion in water under ultraviolet (UV) illumination at 365 nm.

tively. The result implied that the dominant emission was at 488 nm and other emission spectra at 535 and 628 nm were much weaker. Thus, the PL behavior of the C-dots blended NFs was similar to the C-dots and slightly red shifting of the spectra occurred as compared to the pristine C-dots spectra which might be occurred due to the interaction between the available functional groups of C-dots and keratin/PVA NFs. The results indicated a good distribution of very small C-dots in the NFs which was also supported by TEM images (Figure 2(b)-(d)). It was interesting to observe that the PL signal was found to be enhanced noticeably at the wavelength of 488 nm with increasing concentration of C-dots in the order of 0.05, 0.5, and 1.0 wt% as shown in Figure 5(b)(i), (ii), and (iii), respectively. However, it was not strongly occurred at the wavelength of 535 or 620 nm. The spectacular blue-green or cyan color emission was seen during UV-illumination at the wavelength of 365 nm from the keratin/PVA/C-dots NF mat in the presence of different concentration of C-dots before and after immersion in water as depicted in Figure 6. The displayed color was even more vivid after water treatment as demonstrated in the figure. This result indicated that the C-dots were not washed out during transformation of the NFs mat from non-transparent to transparent form through water treatment. Certainly, the C-dots were well distributed and strongly bonded with the NFs and showed good quantum confinement properties of the light emitting particles in the NFs.

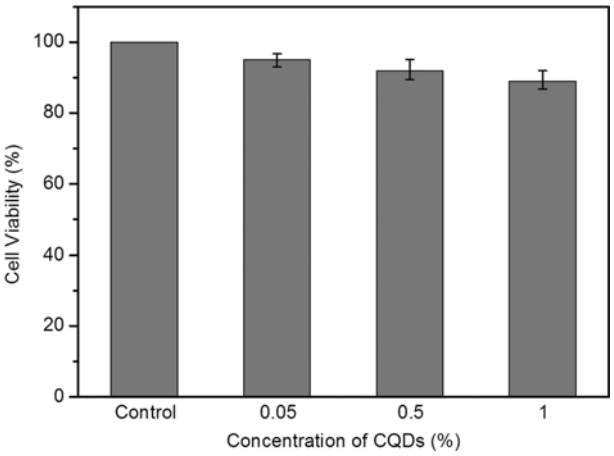

Figure 7. *In vitro* cytotoxicity test of the nanofibers against NIH-3T3 cell for 24 h incubation.

Biocompatibility. The biocompatibility of the keratin/PVA/C-dots NFs mat was evaluated by cytotoxicity experiment against NIH-3T3 cell through MTT assay. The cell viability test data was obtained after incubation of the cells with the composite

NFs mat for 24 h (Figure 7). The number of viable cells on the composite NFs mat was found to be slightly decreased with increasing amount of C-dots as shown in the figure. The results still indicated the considerable biocompatibility of the keratin/PVA/C-dots NFs mat as relative cell viability on keratin/PVA/C-dots mat with 0.05 wt% C-dots was close to ~96% after 24 h exposure. The viability of cell was found to be ~93% and ~90% for 0.5 and 1.0 wt% C-dots present in keratin/PVA/C-dots, respectively. It is well reported that C-dots are nontoxic against living cell even at a reasonably high concentrations[28] and could be safe for *in vivo* applications.[29]

Conclusions

In summary, electrospun keratin/PVA/C-dots composite NFs were successfully prepared by simply adding C-dots in the keratin/PVA polymer solution prior to electrospinning. It was observed that the C-dots were distributed inside the polymer matrix not only without sacrificing their optical properties and disturbing the morphology of NFs but also preserving the optical transparency of the NFs and demonstrated biocompatibility in the living cell environment. This technique provides a convenient way to achieve stable and uniformly distributed C-dots in electrospun nanofiber mats. These results may lead to the development of a new family of advanced composite NFs consisting of C-dots and polymer for different applications such as optoelectronic devices, metal ion detection, and biomedical application such as cell culture and imaging.

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