Synthesis and Properties of Photoluminescent Carbon Quantum Dot/ Polyacrylonitrile Composite Nanofibers

Banafsheh Safaei, Mostafa Youssefi, Behzad Rezaei and Neda Irannejad

Department of Textile Engineering, Isfahan University of Technology, Isfahan, Iran; Department of Chemistry, Isfahan University of Technology, Isfahan, Iran

ABSTRACT
Carbon quantum dot (CQD)/polyacrylonitrile (PAN) composite nanofibers were fabricated using the electrospinning procedure. The composite nanofibers were characterized by scanning electron microscopy, Fourier transformation infrared spectroscopy, UV–visible spectroscopy, fluorescence spectrophotometry, fluorescence microscopy, and reflection spectrophotometry. The produced CQD/PAN composite nanofibers exhibited multicolor emission under different excitation energies, which could be attributed to the presence of CQDs embedded inside the PAN matrix. Fluorescence microscopic images confirmed the uniform dispersion and the photoluminescence behavior of the composite CQD/PAN nanofibers. The produced nanofibers could be easily fabricated and potentially used in a variety of applications like photochemical reactions, biological imaging, and optoelectronic devices.

1. Introduction
In the textile industry, fluorescent brightening agents have extensive application in dyeing strong bright shades on all fibers [1]. However, production of polymer and fiber composites with tunable fluorescence properties has received great attention due to their potential applications in many fields such as biological labels, light-emitting devices, and nonlinear optical devices. [2–6]. On the other hand, Quantum dots (QDs), which are nanocrystalline materials of physical dimensions smaller than the exciton Bohr radius [4,6], have been used for a variety of applications such as energy and optical sensing, optical amplification, fluorescent labeling for medical diagnosis, and bio-imaging. This is due to their specific fluorescence and electrical properties [7]. The electronic properties of quantum dots depend on their size in the nanometer region. Carbon quantum dots (CQDs), which are members of the carbon family, have high chemical stability, high optical absorbivity, biocompatibility, low toxicity, and easy functionalization [8–10]. CQDs can be utilized as a filler in polymer composites because of their high aspect ratio, nanosize, very low density, and excellent optical properties. Many studies have focused on the preparation of polymer/ CQD composite films and determination of their physical
2. Experimental

2.1. Materials

Poly acrylonitrile (PAN), with the weight-average molecular weight (Mw) of 100,000 g/mol, was received from Polyaeryl Company. N, N-Dimethylformamide (DMF) 99.9% was purchased from Merck as the solvent for PAN. Chitosan (\((C_6H_{11}NO_4)n\), with MW of 100000–300000, was got from Acros, and acetic acid 99.9% was received from Merck.

2.2. Synthesis and Characterization of Carbon QDs

CQDs were synthesized from chitosan in accordance with the procedure reported elsewhere [24]. About 2.0-g chitosan was solved in 18-mL acetic acid (2%) and heated at 180 °C for 16 h in a Teflon-coated stainless steel autoclave. After cooling it to room temperature, the obtained dark brown product was centrifuged for 25 min at 14000 rpm to remove the higher size particles with less fluoresce intensity. The brown solution of CQDs was filtered using a 0.22-μ mesh membrane filter. The results of the characterization properties [11–14]. Such nanocomposite materials are used in a variety of applications such as smart clothing, high-performance aircraft, and sensors [12,15,16].

On the other hand, electrospinning, which is a technique capable of producing ultrathin fibers, provides a simple means to produce nanofibers of polymer/QDs for many applications [17]. There are several studies on the preparation of polymer/QDs composite nanofibers and determination of their physical properties [18–21]. In this regard, the main challenge is increasing the dispersion of QDs in the polymer matrix and achieving the desired optical properties of the composite nanofibers. There are few studies on the synthesis and properties of polymer/CQD composite nanofibers; thus, in the present paper, the fabrication of PAN/CQDs composite nanofibers (NFs) by electrospinning process was attempted with different contents of CQDs, with a particular focus on the morphology and the optical properties of the composite nanofibers at room temperature. The produced composite nanofibers with photoluminescent properties could have potential usage in many applications such as Fe ion sensing [22], photocatalyst in wastewater [21], and gas sensor [23] in the future studies.

Figure 1. SEM images of (a) PAN, (b) PAN/1CQD, (c) PAN/2CQD, and (d) PAN/4CQD nanofibers.
of the produced CQDs have been reported elsewhere [25]. The average size of the CQDs used in this study was about 1–10 nm.

### 2.3. Electrospinning

CQDs were dispersed in DMF with the loading of 1.25 mg/mL (PAN/1CQD), 2.5 mg/ml (PAN/2CQD), and 5 mg/ml (PAN/4CQD), respectively. The dispersions were stirred at room temperature for 2 h. The mixture was sonicated using a Fisher Scientific, Model 550, ultrasonic generator at room temperature for 2 h. PAN powder was added to the dispersion at room temperature. The mixtures were stirred at room temperature for 2 h. Then, 1 ml of each DMF/PAN/CQD dispersion was inserted in a 1-ml syringe equipped with a stainless steel hypodermic needle (gauge 23). The syringe needle was connected to a high-voltage generator operating in the positive DC mode with an applied voltage of 15.5 kV. The needle acted as the electrode for the electrospinning process. The dispersions were injected from the syringe pump with a feed rate of 0.11 ml/h, at room temperature for 3 h. Electrospun fiber mats were collected on the rotating drums with the diameter of 15 cm and the rotation speed of 70 rpm.

### 2.4. Characterization

The surface morphology of nanofibers was studied using a scanning electron microscope (SEM, Philips XL30, Netherlands, at 20 kV). In order to determine the average diameter of nanofibers and their distribution, 30 fibers were randomly selected from each SEM image and the diameter of the fibers was measured using an image analysis software. Fourier transform infrared spectroscopy (FTIR) spectra were obtained using a Bomem MB100 spectrometer. Attenuated total reflectance (ATR–FTIR) spectra of the samples were also obtained. UV-vis transmission spectra of the samples were obtained using a TU-1810 UV–vis Spectrophotometer (Pgeneral, China). Photoluminescence emission of the samples was measured using a kind of LS50B Luminescence Spectrometer (Edinburgh Instruments, UK). Fluorescence microscopic images were obtained using an Olympus BX51 fluorescence microscope.

### 3. Results and Discussion

#### 3.1. Morphology

The SEM micrographs and diameter distribution diagrams of electrospun PAN and PAN/CQD composite nanofibers are shown in Figure 1. The average diameters of PAN and PAN/CQD electrospun nanofibers are illustrated in Table 1. It was observed that the morphology and diameter of PAN electrospun nanofibers were significantly affected by CQD loading. The average diameter of PAN/CQD nanofibers varied from 183 to 400 nm. SEM micrographs of PAN and PAN/CQD composite nanofibers showed that

| Samples         | Diameter(nm) | Std. deviation |
|-----------------|--------------|----------------|
| PAN             | 183          | 23             |
| PAN/1CQD        | 203          | 28             |
| PAN/2CQD        | 271          | 27             |
| PAN/4CQD        | 379          | 35             |

![Figure 2. FTIR spectra of (a) PAN, (b) PAN/1CQD, (c) PAN/2CQD, and (d) PAN/4CQD nanofibers.](image-url)
3.2. Fourier Transform Infrared Spectroscopy

The FTIR spectra of PAN nanofibers are illustrated in Figure 2. FTIR spectra of PAN nanofibers had many vibrations and absorption peaks related to the existence of CH2, C≡N, C=O, C−O, and C−H bonds. The absorption peaks in the range of 2932, 1450, and 1080 cm−1 were related to C−H bonds that existed in CH, CH2, and CH3; in this range, one weak peak was observed that was related to C–H bonds too. The peaks could be attributed to the vibrations of different modes in the methylene group of PANS [28]. The peak which appeared at 2245 cm−1 was related to the characteristic nitrile (C≡N) stretching bond, indicating that the nitrile group existed in the polyacrylonitrile chain [29]. The absorption peaks in the ranges of 1730, 1170, 1450, 1370, and 3400 cm−1 were related to the presence of co-monomers in PAN [20]. The absorption band that appeared at 1510 cm−1 for PAN/CQD could be assigned to the bending vibrations of the amide bond (CONH). The peak might be associated with the stretching vibrations of the amide bond (CONH). The FTIR–ATR analysis was performed to investigate the surface functional group of the nanofibers and study the probable CQD and PAN interactions. As shown in Figure 3, the bands at 1530 cm−1 in PAN/CQD nanofibers could be attributed to the bending vibrations of the amide bond (CONH). The peak might be associated with the stretching vibrations of C−N. The FTIR–ATR analysis was performed to investigate the surface functional group of the nanofibers and study the probable CQD and PAN interactions. As shown in Figure 3, the bands at 1530 cm−1 in PAN/CQD nanofibers could be attributed to the bending vibrations of the amide bond (CONH).

3.3. UV–Vis Spectroscopy

Figure 4 presents the UV–vis spectra of PAN/CQD nanofibers. CQDs can show fluorescence properties and absorb the light energy of a specific wavelength, as well as being uniform without any beads. The results also indicated that the average diameter of PAN/CQD composite nanofibers was increased by enhancing CQD loading. It could be due to the increase in the concentration of CQDs in the spinning solution, thereby affecting the viscosity of the solution [26,27]. As reported in the reference [27], there could be also an increase in the electrical conductivity of the spinning solution due to the loading of CQDs. However, it seemed that in our experiments the effect of increasing the viscosity of the electrospinning solutions on the diameter of the nanofibers was dominant when compared with the effect of electrical conductivity of electrospinning solutions.
as re-emitting light at a longer wavelength. They typically show optical absorption in the UV region with a tail extending to the visible range. The UV–vis absorption spectra for PAN/1CQD, PAN/2CQD and PAN/4CQD nanofibers with maximums at 314, 316, and 318 nm are displayed in Figure 4. These absorption bands could be attributed to the π–π* transition of the C=C bonds or the n–π* transition of C=O bonds [32].

3.4. Fluorescence Spectrometry

The composite nanofibers were expected to display photoluminescence because of the presence of CQDs inside the polymer matrix. The photoluminescence emission spectra of the diluted electrospinning solutions of PAN and PAN/CQD are shown in Figure 5. The fluorescence spectra were similar to the reported results from other authors; indicated that the emission wavelengths were dependent on the excitation wavelengths [8,23,25,33,34]. No significant emission within the visible spectrum was observed for the pure PAN electrospinning solution when it was excited at the wavelengths of 350 nm, 477 nm, and 530 nm. However, PAN/1CQD, PAN/2CQD, and PAN/4CQD electrospinning solutions emitted light at the wavelengths of 560, 598, and 660 nm when they were excited at the wavelength of 350, 477, and 530 nm, respectively. These observations are in agreement with the fluorescence microscopic images obtained from the nanofibers. Therefore, it can be seen that with excitation of different wavelengths, the emissions in red, green, and blue regions were observed. The slight difference which was observed in the color of the fluorescence microscopic image (excited at 350 nm) and the fluorescence spectra could be attributed to the medium that surrounded the quantum dots and probable interactions of CQDs and

Figure 5. Emission spectra of PAN/CQDs electrospinning solutions excited at the wavelength of (a) 350 nm, (b) 477 nm, and (c) 530 nm.

Figure 6. Reflection spectra of PAN/CQD nanofiber mats on the (a) white and (b) green standard substrates.
photoluminescence property was not eliminated when CQDs were surrounded by the polymer matrix chains. In other words, PAN/CQD composite nanofiber mats exhibited photoluminescence properties in the visible region of electromagnetic radiations. The results showed that the optical properties of CQDs were preserved inside the composite nanofibers.

3.5. Fluorescence Microscopy

Fluorescence microscopic images were also captured by exciting the samples with three different filters at 350, 477, and 530 nm, as shown in Figure 7. The color emissions
from the nanofiber mats confirmed the uniform distribution of CQDs in the polymer matrix. The photoluminescence behavior of CQDs was well detected inside the PAN/CQDs nanofiber mats. Therefore, the uniformity of the color emissions throughout the electrospun composite PAN/CQD nanofiber mats confirmed the uniform distribution of CQDs without aggregation in the polymer solid matrix. In addition, the characteristic photoluminescence behavior of CQDs was well preserved inside the PAN nanofiber mats.

4. Conclusion

PAN/CQD Composite nanofibers were successfully produced using the electrospinning process. Pure PAN and PAN/CQD composite nanofibers were uniform, without any beads, as revealed in SEM micrographs. FTIR analysis did not show any chemical interaction between PAN and CQDs. The spinning solution, as well as the composite nanofibers, exhibited photoluminescence properties upon excitation by different excitation energies. The results confirmed that the optical properties of CQDs were preserved inside the polymer matrix. The results of reflection spectrophotometry measurements also showed that the light reflection of composite nanofiber mats was higher than that of the pure PAN nanofiber mat, which could be attributed to the photoluminescence properties of CQDs inside the polymer matrix. The uniform photoluminescence behavior of composite nanofibers was well detected inside the PAN/CQDs nanofiber mats by fluorescence microscopic images. To conclude, composite PAN/CQD nanofibers with photoluminescence properties could be potentially used in a variety of applications such as smart clothing, high-performance aircrafts, sensors, photochemical reactions, biological imaging, and optoelectronic devices.

Disclosure Statement

No potential conflict of interest was reported by the authors.

ORCID

Mostafa Yousefi http://orcid.org/0000-0002-3486-9834

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