



Preparation and characterization of optically transparent and photoluminescent electrospun nanofiber composed of carbon quantum dots and polyacrylonitrile blend with polyacrylic acid



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ABSTRACT

Novel photoluminescence (PL) composite nanofibers (NFs) consist of carbon quantum dots (CQDs) and polyacrylonitrile blend with polyacrylic acid (PAN/PAA) were fabricated by the coelectrospinning process. The air-dried CQDs containing NFs were characterized by field-emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), UV-visible spectroscopy, spectrofluorometer, and confocal microscopy. CQDs are familiar to emit blue, green and red color depending on the excitation energy. The PAN/PAA/CQDs NFs were found to be optically transparent and exhibited PL properties similar to CQDs. Therefore, blue, green and red color was observed under confocal microscope from the NFs membrane while the sample was excited by 405 nm, 488 nm and 543 nm lasers. The results indicated the well preserved quantum confinement properties of the CQDs inside the polymer matrix without aggregation or substantial quantum dots growth.

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1. Introduction

Quantum dots (QDs), as nanocrystals, possess tunable optical and electric properties, photochemical stability, and have found wide applications in areas such as energy and optical sensing, optical amplification, and fluorescent labeling [1,2]. Polymer nanocomposites with nanomaterials specially QDs have appealed much concentration because of their unique physicochemical properties and wide potential applications in the field of electronic and optical devices, sensors, electrode materials, smart clothing, membranes, and wound-dressing materials, etc. [3–5]. In fact, the systematic introduction of nanomaterials such as QDs, magnetic nanoparticles, photocatalytic nanoparticles or carbon nanotube in the polymer matrix will not only generate new composite with excellent physicochemical properties but also helps to avoid the aggregation of the particles inside the matrix [6,7]. It is because of

QDs capability to be well-dispersed throughout the polymer nanofibers (NFs) without apparent aggregation within similar solvent environment. Thus Förster resonance energy transfer between neighboring QDs did not occur and the fluorescence properties of the single QDs are preserved [8]. Electrospinning has emerged as a versatile technique capable of processing rich variety of ultra-thin fiber with diameters down to 50 nm and lengths up to a kilometer, providing a straightforward means to produce NFs composite from polymers and QDs or nanoparticles for target application [9].

To date, intense attention has been focused to design and characterize a variety of QDs/polymer nanocomposite such as ZnO/PVA, CdS/PVP, ZnO/poly(vinyl pyrrolidone), CdTe/PVA, CdSe–ZnS/PVA, CdSe–ZnS/PS, TiO₂/PVP, TiO₂/PPV for optical sensing or catalytic sensing [10–16]. The widely synthesized and used semiconductor QDs derived from metallic elements, such as CdS, CdSe, PbSe, CdSe/ZnS, CdSe/CdS etc are environmentally and biologically hazardous which limits their practical application. But carbon quantum dots (CQDs), a new member of the nanocarbon family have been originated to be enthralling QDs for numerous applications owing to their favorable tunable luminescent properties, high chemical stability, low toxicity, biocompatibility, and

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easy functionalization [17]. CQDs display spectrally broad (unstructured) excitation dependent photoluminescence (PL) emission but the origins of PL are not yet entirely understood. The multicolor PL emission of CQDs may arise from the radiative recombination of excitons of carbon, emissive traps, quantum-confinement effect, aromatic structures/oxygen-containing groups, free zig-zag sites or edge defects [18]. In recent years, CQDs have been demonstrated to possess high emission quantum yields up to 60–80% [19]. The multicolor PL emission property of CQD has been used to design excellent opto-electronic devices, fluorescence bio-imaging probes or security-check devices [20–22]. It is already used for making color switchable light emitting diode based on changing the voltage parameter of the devices [19]. There are a lot of reports already available for nanofiber prepared from many different polymer and QDs [10–16]. However, there is no report yet for transparent nanofiber composed of CQDs and polymer specially polyacrylonitrile blend with polyacrylic acid (PAN/PAA).

In the present report, we have described the fabrication of PAN/PAA/CQDs composite nanofibers (NFs) membrane by coelectrospinning process and focused on the optical behavior specially PL properties of the composite at room temperature. The composite NFs were found to be exhibited blue, green, and red color emission similar to that of the CQDs when they were excited with different excitation energy. The results implied the well preserved property of CQDs inside the polymer matrix along with throughout distribution inside the fibers. Therefore, the stemmed composite NFs by the co-electrospinning has shaped a new pathway to transfer special nanoscale effect to macro structure performance in various application fields such as anti-counterfeiting, UV protector, multifunctional textile, optoelectronic devices, biological labeling, and damage detection for composite structures.

2. Experimental

2.1. Reagents and materials

PAN and PAA with average molecular weight of 150,000 g/mol and 250,000 g/mol respectively (Sigma–Aldrich) were used as the polymer matrix and N, N-Dimethylformamide (DMF, 99.9%, Sigma–Aldrich) was employed as the solvent for dissolving PAN and PAA. Urea (99.9%, Sigma–Aldrich), Citric acid (99.5%, Sigma–Aldrich), Ethanol (99.9%, Sigma–Aldrich) was employed for synthesis of CQDs. All the chemicals were used as received.

2.2. Synthesis and characterization of carbon QDs

CQDs were synthesized using microwave assisted pyrolysis method in accordance with the procedure reported elsewhere [23] with some modification. In brief, 1 g citric acid (CA) and 0.5 g of urea was dissolved in a 50 mL vial using 10 mL deionized water before microwave (700W) treatment for 5 min. The obtained dark brown clustered solid was dissolve in ethanol for extracting CQDs. The solution containing CQDs was centrifuged at 5000 rpm for 15 min to remove large or agglomerated particle. The resulting solution was kept overnight in an oven at 80C. Finally the black dried sample was collected, measured and dispersed in DMSO. The brownish solution having concentration 10 and 30 mg/mL was used for further experiment. The as prepared CQDs were identified and characterized by UV-vis spectroscopy (Fig.S-1), transmission electron microscopic (TEM) images and (PL) spectra (Fig.S-2) as shown in supplementary information (SI). The observed information was identical with the reported results [23,24].

2.3. Electrospinning procedure

In a typical experimental procedure, transparent PAN/PAA/CQDs composite NFs were prepared with five steps: (1) Preparation of composite PAN/PAA solutions (DMSO, 7wt%) at weight ratio 1:1; (2) Dilution of the colloidal solution of CQDs to desire volume in DMSO; (3) Preparation of electrospinning precursor solution using 8g PAN/PAA solutions with 10 mg/mL (CQD-10) and 30 mg/mL (CQD-30) of CQDs colloidal solution; (5) Fabrication of composite transparent PAN/PAA/CQDs NFs by electrospinning at room temperature with 75% relative humidity. The applied voltage was 15 KV and the distance between the needle tip and the collector was 15 cm. The feeding rate of the solution was 1 mL/h. Finally, the composite NFs were dried at room temperature in relatively closed environment.

2.4. Sample characterization

The surface morphology of NFs was studied by using a field-emission scanning electron microscope (FE-SEM, Hitachi S-7400, Japan) operated at 1.00 kV electron. TEM images were captured by using Philips Tecnai G2 F20 microscope (Philips, Netherlands) with an accelerating voltage of 200 kV. Fourier transform infrared spectroscopy (FTIR) of samples was recorded on a BRUKER VECTOR-22 spectrometer. Photoluminescence (PL) emission measurements were performed using LS50B Luminescence Spectrometer (Edinburgh Instruments, UK). UV-Vis absorption and transmittance was measured on a TU-1810 UV–Vis Spectrophotometer (Pgeneral, China). The X-ray photoelectron spectroscopy (XPS) measurements were performed on a Thermo Scientific K-Alpha KA1066 spectrometer using a monochromatic Al-K α X-ray source ($h\nu = 1486.6$ eV). Photoluminescence life time decay profile was measured using Time Correlated Single Photon Counting Spectrometer (FLS920, Edinburgh Instruments, UK).

3. Results and discussions

3.1. Characterization of nanofiber

The FE-SEM and TEM images of the electrospun NFs in absence and presence of CQD-10 and CQD-30 were presented in Fig. 1 and Fig. 2 respectively. The surface of the elctrospun PAN/PAA NFs with and without CQDs was not smooth as seen in the FE-SEM images illustrated in Fig. 1. It was also seen that fiber morphology of PAN/PAA NFs in absence and presence of CQDs was not changed apparently.

On the other hand, the presence of CQDs in the composite NFs was confirmed by the TEM images. The corresponding TEM images of PAN/PAA NFs in absence and presence of CQD-10 and CQD-30 was demonstrated in low and high resolution in Fig. 2. The rough surface of the NFs was clearly observed in all cases as shown in Fig. 2. The diameter of the as prepared NFs can be calculated from the scale bar around 300–400 nm. The presence of CQDs in composite NFs prepares from both CQD-10 and CQD-30 was identified inside the fiber and recorded in low and high magnification as shown in Fig. 2 (c-low, and d-high) and Fig. 2 (e-low and d-high) respectively. The CQDs were found to be uniformly distributed inside the fiber structure as shown in both low and high resolution images without aggregation. Higher numbers of CQDs were observed in the composite from CQD-30 (Fig. 2e and f) in comparison with that of the CQD-10 (Fig. 2c and d) as shown in the Fig. 2. The average size of the CQDs used in this study was about 3–5 nm, as demonstrates in the TEM images in Fig. S-2(a).

The Fourier transform infrared spectroscopy (FTIR) analysis was performed in order to investigate the surface functional group of

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