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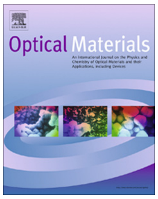

Luminescence properties of silk cocoon derived carbonaceous fluorescent nanoparticles/PVA hybrid film

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ABSTRACT

Carbonaceous fluorescent nanoparticles (CFNs) with broad particle distribution were synthesized by thermal-treatment using carbonation of silk cocoon as raw materials. The experimental results showed tunable emission wavelength of the nanoparticles. The quantum yield of the CFNs was calculated to be 23%. A CFNs/PVA hybrid thin film was prepared from a blend of the CFNs with polyvinyl alcohol (PVA) showing interesting green afterglow which could be observed by naked eyes. The afterglow spectrum revealed that the CFNs/PVA thin film had a broad afterglow emission peak located at 520 nm. The afterglow intensity decay curve of the film showed visually recognizable period longer than 140 s. The PVA–PVA hydrogen bonding in the PVA matrix may play a key role for the afterglow.

1. Introduction

Since the discovery of a new class of carbonaceous fluorescent nanoparticles (CFNs) derived from the single-walled carbon nanotube by arc-discharge methods in 2004 [1], the CFNs have attracted tremendous attention due to their unique properties and potential applications, including fluorescent carbon inks [2], elective detection of metal ions [3], and biological labeling [4], etc. Compared to organic dyes and semiconductor quantum dots, the CFNs are superior in tunable emission [5], low cytotoxicity [6] and high biocompatibility [7]. Thus far, there are two types of synthetic strategies for preparing CFNs. Firstly, the so called top-down strategy summarizes different methods including chemical oxidation [8], hydrothermal [9], arc-discharge [1] and laser ablation [10], where the carbonaceous fluorescent nanoparticles are prepared by smashing a larger crystalline carbonaceous structure into small pieces. In an opposite direction, the bottom–up approaches prepare CFNs by combustion [11], thermal decomposition [12], and dehydration of suitable carbonaceous precursors [13]. However, the above mentioned methods involve intricate processes, expensive starting materials or rigorous experimental conditions which hindered their applications.

Recently, there has been a trend to prepare CFNs using biomass materials as starting materials, such as plant leaf [14], willow bark [15], orange juice [16], and egg [2], due to their low cost, easy acquisition, and nontoxicity. Among the various biomass candidates, silk cocoon, a nontoxic protein-based biopolymer which is composed of fibrous proteins and sericin and has a good biocompatibility, is promising for the preparation of CFNs. Compared with other biomass materials, silk cocoon has much higher nitrogen content (ca. 18.36–18.65%) due to it abundant proteins content [17], which makes it a significant precursor for N-doped CFNs. Li et al. [18] obtained N-doped photoluminescent carbonaceous nanospheres with an average diameter of ca. 70 nm by hydrothermal treatment of cocoon silk at 200 °C for 72 h. Wu et al. [17] prepared 4–7 nm N-doped amphoteric carbon dots from silk in NaOH aqueous solution by hydrothermal treatment at 190 °C for 3 h of which a photoluminescence quantum yield of 13.9% were determined. The as-prepared carbon dots are highly photostable, low toxic and suitable for bioimaging. However hydrothermal treatment requires high pressure, sealed condition, and other strict requirements for the equipment.

Herein, we present an easy and low-cost approach for synthesizing CFNs from silk cocoon through a pyrolysis process. Interestingly, when the silk cocoon based CFNs was incorporated into the polyvinyl alcohol (PVA) matrix, long-lasting afterglow can be seen from the composite film by naked eyes at room temperature after excitation by ultraviolet (UV) light.

2. Experimental

2.1. Preparation of CFNs from silk cocoon

The silk cocoon was firstly washed with distilled water and dried at 60 °C. Then 0.8 g cut-in-piece silk cocoon was heat treated

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in a tube furnace at 300 °C for 4 h in a nitrogen (N_2, 99.999%) atmosphere with a heating rate of 10 °C/min. The resulting pyrolyzed black solids were cooled down to room temperature in the furnace naturally, collected and then grounded in an agate mortar into fine powder. The powder was ultrasonic dispersed in distilled water (the ratio of solid to liquid is 1 g:400 ml) for 30 min, and filtered with a 0.22 μm filtration membrane. The filtered solution was further centrifuged at 8000 rpm for 30 min to obtain a supernatant which contains CFNs.

2.2. Preparation of CFNs/PVA composites thin film

1 g PVA was firstly added into 10 ml distilled water and then mixed with 1 ml of the above-mentioned supernatant under magnetic stirring at 85 °C until the PVA was dissolved completely forming a uniform CFNs/PVA mixture. Then the mixture was poured onto a flat glassplate and then dried at 60 °C forming a thin film. The thin film was peeled off carefully and then annealed in an oven at 100 °C for 30 min.

2.3. Instruments and measurements

Transmission electron microscopy (TEM) observations were performed on a TECNAI 10 (PHILIPS) electron microscope. X-ray diffraction (XRD) patterns were obtained from a XD-2X/M4600 X-ray diffractometer with Cu Kα radiation (40 kV, 20 mA, λ = 1.54051 Å). The Fourier transform infrared (FTIR) spectra were measured by an Avatar 360 FT-IR (Thermo Nicolet) spectrometer using the KBr pellet technique ranging from 1000 to 4000 cm^{-1}. The fluorescence spectra of the CFNs and the CFNs/PVA thin film were measured with Hitachi F-7000 fluorescence spectrophotometer. The UV–Vis absorption spectrum of the CFNs aqueous solution was measured with Shimadzu UV-2550. The afterglow decay curve was obtained at room temperature with PR-305 after the sample was exposed to an irradiation from a 1000 lx standard xenon lamp for 15 min.

3. Results and discussion

3.1. Characterization of the CFNs

The XRD pattern of the CFNs is presented in Fig. 1a. Except for the broad diffusive peak at about 25°, no sharp peaks can be observed in the XRD pattern which confirms the amorphous character of the CFNs. The typical TEM image (Fig. 1b) shows that the CFNs are mostly of spherical shape. Size distribution of the CFNs was analyzed by measuring diameters of about 100 CFNs in TEM images, which is shown in the inset of Fig. 1b indicating a centered diameter of the CFNs is about 7 nm.

Elemental analysis revealed that the CFNs are mainly composed of C (57%), H (3%), and N (15%), The content of C and H is approximately equal to that of most reported CFNs [4,14,18]. The FTIR spectrum of the CFNs as shown in Fig. 2 shows a characteristic absorption bands of hydroxyl groups located at 3480 cm^{-1}, the C—H stretching vibrations at 2937 and 2875 cm^{-1}, and the C═O stretching vibrations at 1666 cm^{-1}. The N—H bending vibrations at 1596 cm^{-1} and the C—H bending vibrations at 1130–1064 cm^{-1} can also be observed. These functional groups are produced from the degradation of a wide range of amino acids from silk cocoon, which can improve the hydrophilicity and stability of the CFNs in an aqueous system.

The quantum yield (Q) of the CFNs was calculated by comparative method using Eq. (1), in which Q is the quantum yield, I is the measured integrated emission intensity, n is the refractive index, and A is the optical density. The subscript R refers to the reference fluorophore with known quantum yield. Quinine sulfate in 0.1 M H_2SO_4 with reported quantum yield of 54% at 360 nm was chosen as a standard reference. The obtained results are listed in Table 1. The quantum yield of CFNs in this work is higher than some reported biomass based CFNs [14,17,19]. The relatively high quantum yield of CFNs may caused by the relatively high N content, which is consistent with other reported results that the CFNs with nitrogen groups can significantly enhance their PL properties [15,19–21].

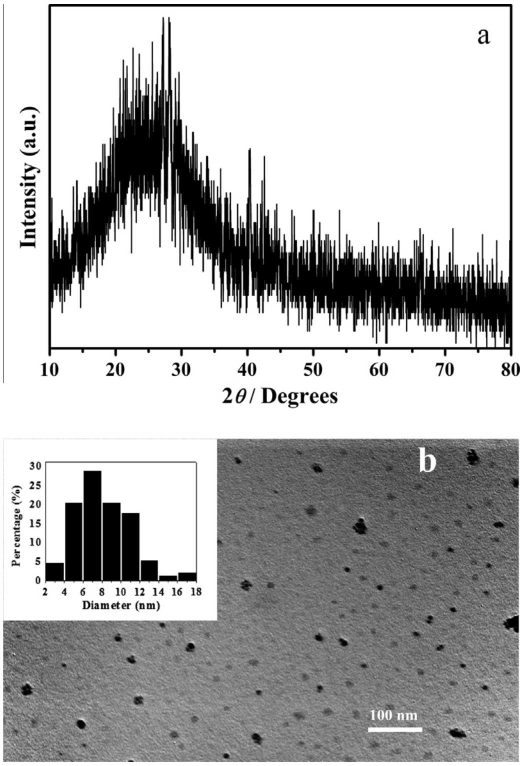

Fig. 1. (a) XRD pattern of the CFNs and (b) TEM image of the CFNs. The inset histogram in (b) is size distribution of the CFNs measured by TEM.

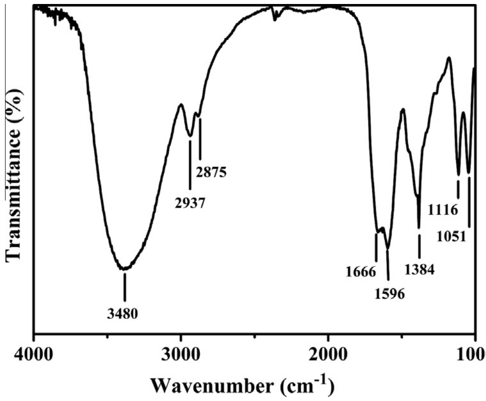

Fig. 2. FT-IR spectrum of the as-prepared carbonaceous fluorescent nanoparticles.

$$Q = Q_R \frac{I}{I_R} \frac{A_R}{A} \frac{n^2}{n_R^2} \tag{1}$$

3.2. Photoluminescence properties of the CFNs

The UV–Vis absorption spectrum of the CFNs is shown in Fig. 3a. Two weak absorption bands, one located at about 280 nm and