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Efficient resistance against solid-state quenching of carbon dots towards white light emitting diodes by physical embedding into silica

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ABSTRACT

To overcome self-quenching of carbon dots (CDs) in solid state and provide a universal strategy for efficient luminescence of CDs in solid state, this paper reports a novel method of physical embedding of solid-state CDs into a silica matrix. CD/silica composites were prepared through injecting *N*-(3-(trimethoxysilyl) propyl) ethylenediamine into a CD aqueous solution and have exhibited a high quantum yield of 41.72%. A mechanism of photoluminscence (PL) quenching in solid-state CDs and PL resuming in CD/silica composites was proposed. These CD/silica composites possess excellent film-forming ability, thermostability and ultraviolet (UV) stability. By taking advantage of these remarkable properties, a white light-emitting diode was constructed by combining CD/silica film with a UV chip, which has exhibited warm white light emission with Commission Internationale de L'Eclairage coordinates of (0.44, 0.42) and correlated color temperature of 2951 K. It is evident that CD/silica composites have superior potential in solid-state lighting system.

1. Introduction

White light-emitting diodes (LEDs) are attracting a great deal of attention and their commercialization is expanding to high-volume applications, including general illumination and displays, owing to the merits including efficient lighting, environment-friendly nature and long operational life [1]. Fluorescent carbon dots (CDs), as emerging quantum dots, are intriguingly increasing attention for their outstanding properties, such as excellent fluorescence, photostability, and low toxicity, which make them a promising color converter for application in white LEDs [2,3]. However, strong luminescence quenching in solid-state CDs and lack of long-wavelength emission (in orange and red light regions) in CDs greatly hinder the development and application of CDs-based white LEDs.

To support white LEDs, CDs are needed to emit light in solid state, but most of CD-related studies have been focused on fluorescence of CD solution. Therefore, it is of great significance to explore the solid-state fluorescence of CDs [4,5]. At present, CD-based LEDs are still not satisfactory in their performance owing to strong luminescence quenching in their solid aggregate state [6,7]. Usually, dispersant is needed to realize luminescence in solid-state CDs. Recently, an approach of embedding CDs in solid matrices, such as starch, salts and barium sulfate has been adopted in order to avoid solid-state fluorescence quenching and realize solid-state luminescence of CD-based composites [8–10]. Although the strong photoluminscence (PL) emission of CDs is well preserved in the solid state, curing agent must be further added into CD-based composites to fabricate LEDs [8]. Other several methods have also been proposed, where CDs were embedded in polymer matrices, such as polyvinyl alcohol and polyvinyl pyrrolidone [11,12]. However, polyvinyl alcohol and polyvinyl pyrrolidone are solid powder and need to be heated to form colloids to disperse CD powder. In addition, silica coating has been reported to realize the solid PL of perovskite quantum dots (QDs), in which perovskite QD/silica composites were formed in one-pot synthesis by covalently bonding silica and perovskite QDs [13]. Furthermore, to the best of

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our knowledge, although solid PL of CDs has been realized by combining with curing agent in some reports, there is rare, if any, report on the PL of same CDs in different systems (CD solution, CD powder and CD/curing agent composites). Thus, it is a challenge to explore a novel physical embedding method to realize the solid-state PL on the basis of the elucidation of the mechanism of solid-state PL of CDs. Meanwhile, the film-forming ability of CDs is also expected without additional curing agent.

On the other hand, in most cases, CDs exhibit broadband luminescence with maxima in blue–green region. For warm white LEDs requiring correlated color temperature (CCT) of 2700–4000 K [14], effective synthesis methods and convincing luminescence mechanisms are essential for CDs to realize long wavelength emission [15,16]. Although Qu et al. pointed that large particle sizes and high nitrogen contents are responsible for the efficient red emission [17], the specific mechanism about long-wavelength emission of CDs is still obscure. Therefore, it is also important for CDs to realize efficient orange or red luminescence for the fabrication of warm white LEDs and further explore the mechanism about long-wavelength emission of CDs.

This paper presents a new and effective technology for solid-state PL and film-forming CDs in order to prevent the self-quenching of CDs in solid state. *N*-(3-(Trimethoxysilyl) propyl) ethylenediamine (KH-792) was chosen as the precursor simultaneously for silica matrix as disperse agent and for silanol as film-forming agent. CD/silica composites were formed by direct injection of KH-792 into a CD aqueous solution. In this way, the silica matrix was formed fastly and CDs were embedded into silica by physical doping between CDs and silica. This novel approach has three advantages in realizing solid-state luminescence of CDs applied in LEDs. (1) KH-792 hydrolyzes and polymerizes into the silica, and CDs are further embedded into silica matrix to form CD/silica composites. Thus, these CD particles in CD/silica composites keep an appropriate distance away from each other so that the solid quenching can be restrained. (2) The as-prepared CD/silica composites can be directly tuned into a fluorescent film only through a simple heat-treatment without using any other curing agent. The fabrication process is simple and easy to scale up [18]. (3) The hydrolysis product of KH-792 has no observable absorption between 350 and 750 nm (proved below, Fig. 5h), so the matrix absorbs neither excitation light to CDs nor the emission from CDs, and optical properties of CDs can be unaffected after the solidification. CDs with orange-to-red fluorescence in an ethanol solution were synthesized by the reaction of *p*-phenylenediamine (PPDA) in ethanol medium using a one-step solvothermal process with reaction time being adjusted from 12 h to 6 h by optimization of reaction parameters [19]. Nevertheless, the CD powder directly derived from CD solution suffered fluorescence quenching from their aggregated states. Followed by dispersing the solid CDs in KH-792 aqueous solution, newly formed CD/silica composites showed resumed PL emission. The CD/silica film from heat-drying of CD/silica aqueous solution also reserved PL emission. Then, CD/silica film was combined with ultraviolet (UV) chip to fabricate a white LED. Fig. 1 illuminates schematic diagram of synthesizing CDs and CD/silica film along with the application in white LEDs.

2. Experimental

2.1. Chemicals and materials

PPDA was purchased from Xingfu Fine Chemical Research Institute (Tianjin, China). KH-792, ethanol absolute and methylene dichloride were offered from Guangfu Technology Development Co., Ltd (Tianjin, China). Methanol anhydrous was obtained from Tianli Chemical Reagent Co., Ltd (Tianjin, China). Petroleum ether was provided from Fuchen Chemical Reagent Factory (Tianjin, China). All chemicals were used without further purification.

2.2. Synthesis of CDs

CDs were synthesized according to a solvothermal method reported previously [19]. Typically, PPDA (0.45 g) was dissolved in 45 mL of ethanol to form a transparent solution, which was sealed into a 100 mL poly (tetrafluoroethylene)-lined autoclaves followed by a solvothermal treatment at 180 °C for 6 h. After the reaction, the color of the solution was turned into dark red. This solution including CDs and by-products was critically separated through silica column chromatography using a mixture of methylene chloride and methanol (volume ratio = 30/1) as eluent because CDs and by-products have different polarities. Finally, bright orange-red fluorescent CDs were obtained after removal of solvent under vacuum.

2.3. Preparation of CD/silica composites

CDs (2 mg) were dissolved in 2 mL of water, and then 500 μL of KH-792 was added into the solution under sonication for 3 minutes to form a homogenous solution. The CD/silica film was obtained by a facile heating (80 °C) using quartz chip as substrate, and the CD/silica powder was obtained through a facile heating (80 °C) using a centrifuge tube as substrate and a grinding process for further characterization.

2.4. Fabrication of white LEDs

A white LED was fabricated by using the CD/silica film as luminescent materials and UV chip with the peak emission wavelength centered at 365 nm as LED base. Typically, 40 μL of CD/silica solution was transferred onto the inner wall of the optical lens, and the combined package was treated in a drying oven at 80 °C. Finally, the optical lens were capped on UV chip.

2.5. Characterization

Transmission electron microscopy (TEM) and high resolution TEM (HRTEM) images were taken on a JEOL JEM-2010 microscope. The TEM specimens were prepared by sonicating CD and CD/silica ethanol solutions and depositing a few drops of the solutions onto a carbon-coated copper grid, followed by drying in the oven. Atomic force microscopy (AFM) images were obtained using an NSK SPA-300 H V microscope. The AFM specimens of CD/silica composites were prepared by depositing a few drops of CD/silica solution on a quartz surface. Electrospray ionization mass spectrometry (ESI-MS) analysis was performed on a Bruker micrOTOF-Q III, in which the CDs were dissolved in ethanol with an infusion rate of 3 μL/min. X-ray photoelectron spectroscopy (XPS) measurements were conducted on a Kratos AXIS ULTRA DLD X-ray photoelectron spectrometer with mono X-ray source Al Kα excitation (1486.6 eV). Fourier transform infrared (FT-IR) spectra were obtained from a BRUKER TENSOR 27 spectrometer in the form of KBr pellets. Thermo-gravimetric (TG) curves were measured on a NETZSCH TG 209 F3 with a heating rate of 10 °C per minute under nitrogen. Elemental analysis (EA) measurements were conducted on an ELEMENTAR vario EL cube. Ultraviolet visible (UV–vis) absorption spectra were recorded on a Hitachi U3900 UV–vis spectrophotometer. PL spectra were collected on a Horiba Fluoromax-4 luminescence spectrometer using a Xe lamp as excitation source. The fluorescence decay status and lifetime were obtained on an Edinburgh FLS 980 spectrometer. A spectra scan PR 655 photometer was applied to analyze the emission spectra, Internationale de