Materials Letters 143 (2015) 290–293

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

Highly luminescent carbon nanoparticles as yellow emission conversion phosphors

Xuegang Zheng [a,b,c], Hailong Wang [a,*], Qian Gong [b], Lichun Zhang [d], Guangliang Cui [c], Qingshan Li [d], Li Chen [c], Fuquan Wu [a], Shumin Wang [b]

[a] Provincial Key Laboratory of Laser Polarization and Information Technology, Department of Physics, Qufu Normal University, Qufu 273165, China
[b] State Key Laboratory of Functional Materials for Informatics, Shanghai Institute of Microsystem and Information Technology, Shanghai 200050, China
[c] Institute of Condensed Matter Physics, Linyi University, Linyi 276005, China
[d] School of Physics and Optoelectronic Engineering, Ludong University, Yantai 264025, China

ARTICLE INFO

Article history:
Received 20 September 2014
Accepted 29 December 2014
Available online 7 January 2015

Keywords:
Carbon materials
Nanoparticles
Yellow emission
Phosphors
White light emitting devices

ABSTRACT

We report the novel synthesis of luminescent carbon nanoparticles (CNPs) and their applications as yellow emission conversion phosphors. CNPs were obtained in a hydrothermal process using hexamethylenetetramine (HMT)/glucose mixed solution as precursor. The mixed glucose is found to facilitate the decomposition of HMT, which leads to rapid and low-temperature growth of CNPs. CNPs (quantum yield exceeding 58%) solutions exhibit strong blue-green emission with ultraviolet light illumination and possess typical excitation-dependent photoluminescence (PL) behavior. CNPs were also coated onto ultraviolet and blue LEDs. Broad yellow emission was both achieved with ultraviolet or blue light excitation, indicating such CNPs phosphors can be used in fluorescent lamps or white LEDs. The nontoxic nature and broad yellow emission indicates potential applications of CNPs for phosphor-based white light-emitting devices.

1. Introduction

The development of white light emitting devices is very important in liquid-crystal displays, full-color displays, and normal lighting sources in our life [1]. Generally, three kinds of white light emitting devices have been proposed including incandescent light bulbs, fluorescent lamps and white LEDs, among which fluorescent lamps are widely used as normal lighting source due to high efficiency and low cost, but waste fluorescent lamps often give rise to serious environmental problems. Phosphors containing rare-earth metals (such as YAG:Ce or Sr_3SiO_5 phosphors) are toxic. It can be anticipated that if a new nontoxic alternative can completely or partially replace conventional rare-earth phosphors, environmental issues aroused by rare-earth metal are expected to be greatly minimized. In recent years, people paid much attention on carbon nanomaterials such as carbon nanotubes, graphene and CNPs. Carbon materials is environmentally and biologically compatible, low-cost and chemically stable [2]. There have been some successful demonstrations on CNPs as color-converted phosphors [3–5]. Once CNPs are successively used as the alternates to the traditional heavy-metal-based quantum dots in white-light conversion phosphors, a revolution in lighting will be coming.

To be power-efficient phosphors, CNPs with three key features must be apparent, involving: (1) easy handling, rapid and low-temperature growth; (2) high quantum yield; (3) broad yellow emission spectra. To this date, CNPs have been prepared by various methods, including laser ablation [6,7], electrochemical exfoliation [8], combustion thermal oxidation [9], supported synthetic [10], microwave assisted hydrothermal dehydration of carbohydrates [11,12]. In contrast, decomposition of organic compounds using hydrothermal method is likely to be extended significantly in the mass production of CNPs. Various carbohydrates are used for CNPs production. Tang et al. [5] reported glucose-derived graphene quantum dots, but the quantum yields were as low as to be 7–11%. Earlier times, we used hexamethylenetetramine (HMT) as single precursor to grow fluorescent carbon nanospheres with quantum yield of 35% [3]. In this article, we investigated the growth of fluorescent CNPs using HMT/glucose mixed solution as precursor for the first time. Rapid and low-temperature fabrication of CNPs was demonstrated with the help of adding glucose. The quantum yield is as high as 58.3%. We also obtained broad yellow emission using CNPs as yellow conversion phosphors excited by ultraviolet or blue light.

* Corresponding author. Tel./fax: +86 5375051321.
E-mail address: phyhlwang71@126.com (H. Wang).

http://dx.doi.org/10.1016/j.matlet.2014.12.138
0167-577X/

2. Experimental

2.1. Sample preparation

All chemicals were purchased from Alfa Aesar. HMT and HMT/glucose mixed solution (100:1molar ratio of HMT: glucose) were respectively prepared and transferred into a 50 mL hydrothermal reactor. Distilled water was used as solvent. The reactors were heated in a thermostatic oven and kept at 160 °C or 99 °C for 3 h. Subsequently, the reactor was cooled to room temperature and the solution was removed out from the vessel for characterizations. To demonstrate the yellow light conversion, a few drops of concentrated CNPs solution were coated onto commercially LEDs. The applied voltage for the LEDs was 3.2 V.

2.2. Characterizations

We performed Transmission electron microscopy (TEM) measurements on JEOL, JEM-2100 F with an accelerating voltage of 200 kV. Fluorescence emission and excitation spectra of CNPs aqueous solution were recorded using a Cary eclipse fluorescence spectrophotometer with Xe lamp as an excitation source. The UV-vis spectra were obtained on a Shimadzu UV-3600 UV-vis spectrophotometer. The quantum yield was measured according to the established procedure [13]. Absolute values were calculated using the standard reference sample of Rhodamine B solution known as 0.9 while diluted with distilled water. Fourier transform infrared (FTIR) spectra were obtained by Nicolet 560 spectrometer.

3. Results and discussion

Fig. 1a shows the obtained CNPs solutions from HMT or HMT/glucose mixed solution. Judged by the changes of solutions color, the mixed glucose was found to facilitate the decomposition of HMT and CNPs growth. The formation of CNPs is schematically shown in Fig. 1b, involving rings opening, carbonization, nucleation, growth of carbon dots and aggregation. HMT is rather stable with an admantane-like structure [14], and Glucose in water exhibits closed (ring) forms and is also stable. While HMT and glucose were mixed and heated, the amine derived from HMT will react with the aldehyde group of glucose and forms azomethine [15]. With chain-like structure, azomethines are not stable during heating, which leads to the rapid and low-temperature synthesis of CNPs. The quantum yield of 58.3% was obtained for those CNPs synthesized at 160 °C, which is higher than those synthesized at 99 °C or produced by other precursors [4,5,16]. We also performed TEM measurements with or without glucose as precursor. Fig. 1c shows TEM image of CNPs synthesized from HMT at 160 °C for 3 h. The spherical CNPs have a size distribution of 260–300 nm in diameter. We have explored other different precursors to grow CNPs by the same hydrothermal method, but such large submicron-scale carbon spheres have not been obtained. We do not fully understand the detailed formation mechanism, but we think it is related with the unique characteristics of HMT [3]. Fig. 1d shows TEM images of CNPs synthesized from HMT/glucose at 160 °C, revealing overlapping spherical shapes with a size of 30 nm in diameter. The high-resolution TEM image (Fig. 1d, inset) shows the carbon spheres composed of ~2nm carbon dots. The rapid decomposition of HMT

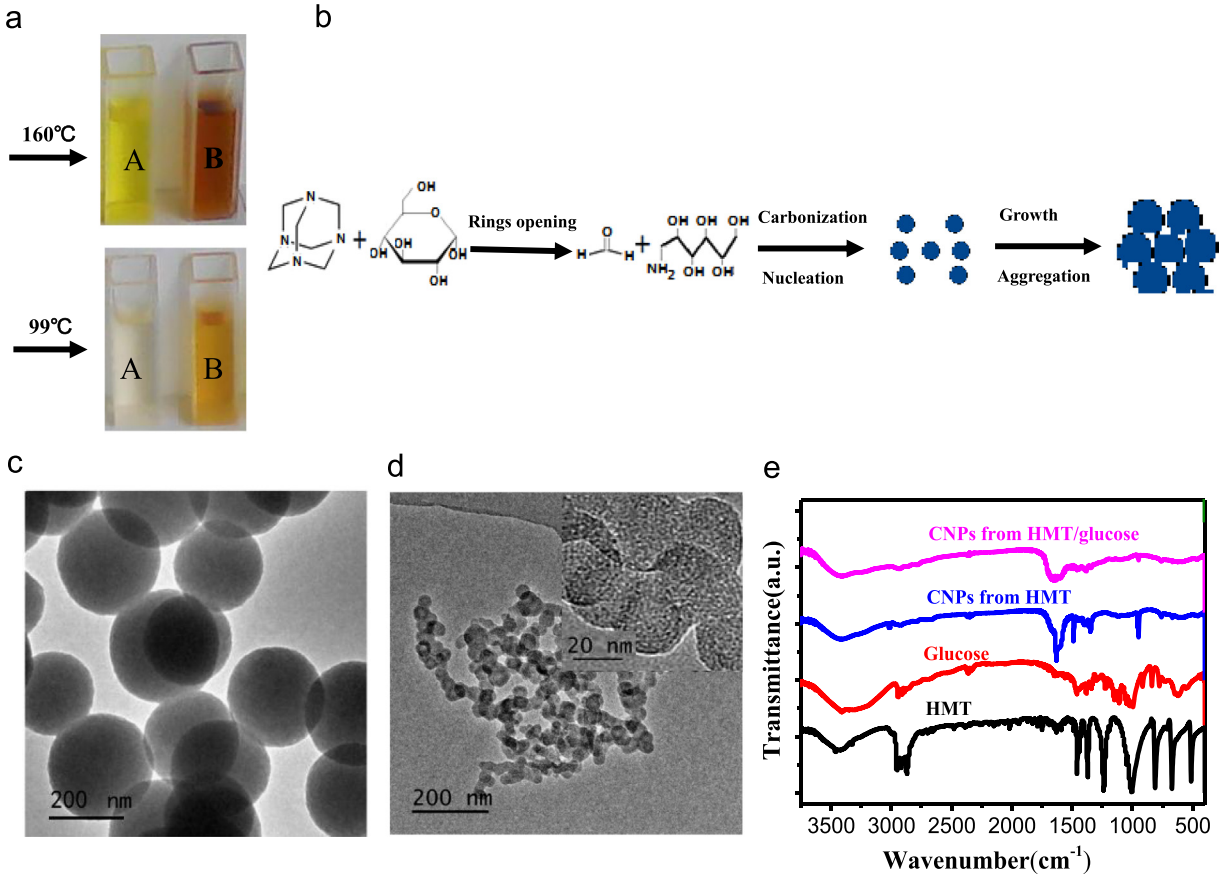

Fig. 1. (a) Photographs of CNPs solutions with white light illumination. A and B correspond to HMT solution and HMT/glucose mixed solution heated at 160 °C or 99 °C for three hours. (b) Scheme for the formation of CNPs by hydrothermal method. (c) TEM image of CNPs synthesized from HMT. (d) TEM images of CNPs synthesized from HMT/glucose. The inset: high-resolution TEM image. (e) FTIR spectra of different samples, including HMT, glucose and CNPs synthesized from HMT or HMT/glucose.