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Template-less synthesis of hollow carbon nanospheres for white light-emitting diodes

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ABSTRACT

A novel approach is demonstrated on the synthesis of hollow carbon nanospheres (HCNs) and their applications as color converter for white light-emitting diodes. HCNs were synthesized in a hydrothermal process using hexamethylenetetramine as precursor. The synthesis involves a template-less and one-step aqueous method for the first time, which enables the growth of HCNs with the temperature as low as 160 °C. HCNs solutions exhibit strong yellow-green emission under ultraviolet light excitation and possess typical excitation-dependent photoluminescence (PL) behavior as carbon nanoparticles. We also used a facile coating method to coat a blue LED with HCNs layer which plays a role as color-converted phosphor. The LED shows bright white light, and the spectrum involves two main components, one from the blue LED chip centered at 455 nm and one from HCNs centered at 520 nm.

1. Introduction

It is well known that the development of white light-emitting diodes (LEDs) has been the subject of intense academic research for years because of their great potential in lighting and display [1]. Usually, a blue LED coated with yellow light-emitting phosphor may generate white light. Two types of most conventional phosphors contain rare-earth metals (such as YAG:Ce or Sr_3SiO_5 phosphors) or organic fluorescent materials(such as dyes or conjugated polymers). However, rare-earth metals have obvious defects such as high cost and toxicity, and organic fluorescent materials have low chemical and thermal stability [2]. As is well known, carbon based fluorescent nanomaterials are environmentally and biologically compatible, low cost and stable chemical properties [3], which may give rise to very promising applications. Once carbon nanoparticles (CNPs) are successively used as white-light-conversed phosphors in production, many problems such as resource shortage and environmental issues are expected to be resolved, and a revolution in white lighting will occur. Recent advances in the research on CNPs, however, mainly focused on its biological and chemical applications, and only a few reports [4,5] paid attention to its potential applications as nontoxic alternates to traditional heavy-metal-based quantum dots in white-light conversion phosphors. The widely accepted mechanism for luminescence of CNPs is the presence of surface energy traps, which become emissive upon surface passivation [6], so it can be anticipated that CNPs with higher surface-to-volume ratio have stronger luminescence, such as hollow carbon nanospheres (HCNs). But till today, there have been no reports on HCNs as color converter for white light-emitting diodes.

The synthesis of HCNs have inspired great interest due to their potential applications in catalyst supports, fuel cells, gas storage and separation, and lithium-ion batteries, which result from high surface-to-volume ratio and high structural stability [7]. Typically, HCNs is synthesized by coating a carbon precursor on a hard template core, followed by hydrothermal carbonization and core removal to obtain hollow carbon nanospheres, which is called templating approach. To remove the template core usually needs thermal treatment at high temperature. Tang et al. [8] reported the removal temperature of latex template as high as 1000 °C, and Xu et al. [9] demonstrated to obtain HCNs at 400 °C, which is the lowest reported growth temperature to this date. In our ideas, however, the growth temperature may be greatly lowered if the templates are not used. Moreover, template-less synthesis of HCNs will reduce growth procedures and make the growth process simple and low-cost. In this paper, we investigated for the first time the template-less synthesis of HCNs at low temperature. HCNs were one-step hydrothermal synthesized by using hexamethylenetetramine as precursor. We also reported HCNs as color converter for white light-emitting diodes using a novel coating method.

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2. Experimental

Synthesis of fluorescent HCNs: All chemicals were purchased from Alfa Aesar. Hexamethylenetetramine solution with the concentration of 10 wt% was prepared by using deionized water as solvent. 35 mL of the solution was put into a hydrothermal reactor with tightened cover. The volume of the glass bottle is 50 mL. The reactor was heated in a thermostatic oven for 3 h at 160 °C. Subsequently, the reactor was cooled to room temperature and the solution was removed out from the vessel for characterizations. To demonstrate the white light emission of HCNs by converting blue light, a commercially waterproof blue LED was placed in the reactor and immersed in the solution at the beginning of the hydrothermal reaction. After the reaction, the blue LED was found to be coated with a yellow layer. The applied voltage and current for the LED were 3.2 V and 30 mA, respectively.

Characterizations: Transmission electron microscopy (TEM) measurements were performed on JEOL, JEM-2100F at operating voltage of 200 kV. Emission spectra of the HCNs solution and the LED were recorded using a Cary eclipse fluorescence spectrophotometer with Xe lamp as an excitation source. The UV–vis spectra were recorded at room temperature on a Shimadzu UV-3600 UV–vis spectrophotometer.

3. Results and discussion

Hexamethylenetetramine reacts with water in the heating process as follows [10]:

$$C_6H_{12}N_4+6H_2O\rightarrow 6HCHO+4NH_3\ (g)$$

Formaldehyde, as one of the carbohydrates which contain C, H, and O in the ratio of 1:2:1, may dehydrate and used as carbon source to prepare CNPs under hydrothermal condition [5]. Fig. 1a and b shows the transmission electron microscopy (TEM) image of HCNs, which clearly reveals relatively spherical shape with a size distribution of 260–300 nm in diameter. The overlapping shadow of the adjacent nanospheres indicates the hollow structure. To the best of our knowledge, no reports have been reported on the template-less preparation of HCNS. The templating approach based on the use of solid molds needs multiple procedures. Especially, high temperature is usually needed to remove the template core through thermal treatment, which also requires the protection of an inert gas atmosphere. Template-less synthesis of HCNS can just avoid these shortcomings. In our study, HCNs were one-step obtained in a hydrothermal process, so the growth process is simple and low-cost. Without the high-temperature

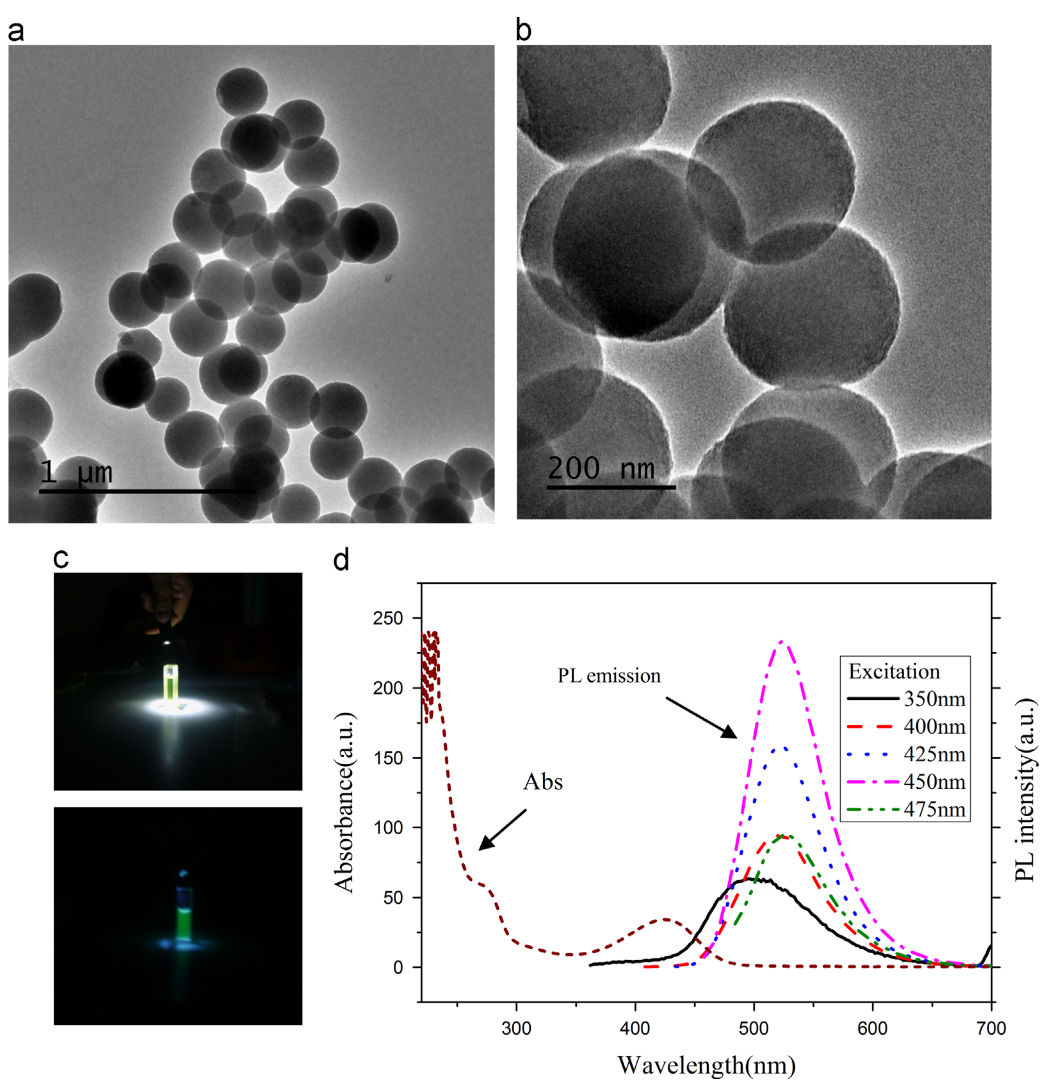

Fig. 1. (a) and (b) TEM images of HCNs. (c) HCNs solution optical images under white light (above) and UV light (below). (d) UV–vis spectrum (left) and PL spectra of HCNs solution (right). (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)