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Easy synthesis of silver nanoparticles-orange emissive carbon dots hybrids exhibiting enhanced fluorescence for white light emitting diodes

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ABSTRACT

Ag nanoparticles (NPs) show a excellent surface plasmon resonance (SPR), which is expected to enable fluorescence enhancement. In this study, a facile approach is proposed for fabrication of Ag NPs/long-wavelength carbon dots (Ag-LCDs) hybrids, wherein Ag NPs work as a fluorescent reinforcer to enhance photoluminescence (PL) intensity of LCDs. The largest enhancement was acquired through adjusting the volume ration between Ag NPs and LCDs. In this process, PL decay is considered as an important and simple characterization to speculate the metal enhanced fluorescence (MEF) mechanism. On the basis of result of small reduction in lifetime, we proposed that the mechanism may be predominantly derived from the localized effectric field effect and partly from the intrinsic radiative decay rate. Moreover, spin-coating technology was utilized to produce LCDs and Ag-LCDs hybrids films. Then, white light-emitting diodes (white LEDs) were constructed by these films with controllable thicknesses and GaN chips. The constructed white LED presented excellent optical performances with an optimal color coordinates (CIE) of (0.33, 0.35), a color rendering index (CRI) of 74.6, a correlated color temperature (CCT) of 5435 K. Notably, the existence of Ag NPs enable these LCDs to improve the luminous efficacy (LE) from 32.63 lm W^{-1} to 41.26 lm W^{-1}. Such superior optical merits enable them the promising potentials for application in optical devices.

1. Introduction

Recently, carbon dots (CDs) have drawn considerable attention due to their fantastic and unique properties, including stable photoluminescence (PL), easy functionality [1,2], and electron transfer behavior compared with tradition luminescent species [3]. After the pioneering report by Xu and co-workers [4], CDs have been produced from a variety of carbon precursors, and present a widely potential application in optoelectronic devices, sensors, photocatalysis and so on [5,6]. However, according to the most reports, the PL intensity of the long-wavelength (in orange and red light regions) CDs (LCDs) are relatively low owing to lack of valid synthesized approach and vague luminescence mechanism, which is a serious impediment to the development and applications [7,8]. For example, owing to the lack of long-wavelength emission and weak absorption in the visible region, short-wavelength CDs (SCDs) can not be utilized directly for phosphor-converted white light diodes (LEDs), photocatalysis [9,10]. Hence, it is high time to establish effective method to improve the PL intensity of LCDs. Metal enhanced fluorescence (MEF) has emerged rapidly as a technology to improve the PL intensity [11–13]. It has been generally exploited to enhance the PL intensity of quantum dots, dyes, lanthanide nanocrystals as well as CDs. The PL enhancement in this study can be derived from the mechanism of surface plasmon resonance (SPR).

Ag-CDs hybrids have been extensively investigated in virtue of their individual properties [3,14,15]. Hyosung Choi et al. found that due to the SPR effect of Ag NPs, current efficiency and luminous efficiency of Ag-CDs hybrids based on polymer LEDs were significantly improved [3]. Efficient surface-enhanced Raman scattering properties were also demonstrated by introducing Ag NPs into CDs [14–16]. However, to the best of our knowledge, few studies have

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been involved to the Ag-enhanced fluorescence of SCDs, not to mention any further improvement of LCDs and their application in white LED. Generally, core-shell structure is preferred to acquire a better MEF effect, which is comprised of noble metal nanostructure, such as metal core or shell, a certain thickness of dielectric layer including silica or polymer and a luminescent species. For instance, research showed that tetraethoxysilane (TEOS) served as silica-shell and controlled the distance between Ag NPs and fluorescent SCDs, which give rise to a more than four-fold increase in PL intensity of SCDs [16,17]. Nevertheless, these fabrication processes are very time consuming and tedious. Interestingly, it was found that SCDs with a green luminescent emission displayed an optimal fluorescence owing to the addition of well-dispersed Ag NPs around the SCDs. Herein, Ag NPs were achieved by the reduction of Ag^+ [18]. The work offered a facile and convenient way to promote PL intensity of SCDs, which stimulated the interest of study on Ag-induced improvement of LCDs.

In the present work, we synthesized the Ag-LCDs hybrids via a simple chemistry method. Herein, we used LCDs as luminescent species and Ag NPs as a fluorescent intensifier to enhance PL intensity. Furthermore, according to the small reduction in lifetime, we proposed that Ag-enhanced PL intensity could be both attributed to the increase of the local field and the intrinsic radiative decay rate. Moreover, the films consisting of LCDs/Ag-LCDs and ultrathin quartz glass were gotten by spin-coating technology. White LED was finally fabricated by combining the GaN and these films. Importantly, the Ag-LCDs present stronger PL intensity, which further increase the luminous efficacy (LE). Thus, the work affords new opportunities to apply them in white LEDs.

2. Experimental

2.1. Materials

Anhydrous citric acid, N-(β-aminoethyl)-γ-aminopropyl methyldimethoxy silane (AEAPMS), silver nitrate ($AgNO_3$, 99.8%), sodium citrate tribasic dihydrate (TSC, 99%), sodium borohydride ($NaBH_4$, 99%) were purchased from Aladdin Chemistry Co.Ltd (Shanghai, China). All the chemicals used in the experiments were of analytical grade and used as received without any further purification.

2.2. Sample preparation

2.2.1. Synthesis of Ag nanoparticles

The Ag NPs solution was synthesized by a one-step reduction method at room temperature according to a previous report [19]. Briefly, an ice-cold freshly prepared solution of $NaBH_4$ (0.25 mL, 100 mM, 250 μL) was rapidly injected into the 24.75 mL aqueous solution containing $AgNO_3$ (0.05 M, 50 μL) and TSC (75 mM, 0.5 mL) under vigorously stirred in air. Afterwards, the obtained colorless solution turned to yellow immediately, which indicated the formation of Ag NPs (0.0108 g/L). It was also notable that no color change and aggregation were observed for the Ag NPs after storage for many months.

2.2.2. Synthesis of LCDs

In our experiments, we synthesized LCDs (centered at 610 nm) from carbon source anhydrous citric acid utilizing a one-pot hot injecting method with a little improvement [20,21,37]. In a typical procedure, 60 mL of AEAPMS were added to a three-necked flask and heated at 220 °C under the protection of a nitrogen atmosphere. Then, 3.0 g of citric acid dissolved uniformly in 6 mL of ethanol was quickly injected into the AEAPMS with vigorous stirring. After 5 min, the color of the solution changed from colorless to light red and then gradually to dark brown, indicating the generation of the LCDs.

2.2.3. Synthesis of Ag-LCDs hybrids

In this work, a simple and straightforward method was established to enhance PL intensity of LCDs. The Ag-LCDs hybrids could be obtained by adding varying volume Ag NPs solution (0.0108 g/L) into 3 ml LCDs. The volume of 0.6 mL, 0.8 mL, and 0.9 mL respectively were labeled as A-LCDs, B-LCDs, C-LCDs hereafter. The schematic synthesis for the LCDs, Ag NPs and Ag-LCDs hybrids are shown in Fig. 1.

2.2.4. Construction white LEDs

Spin-coating technology was obtained to caste the Ag-LCDs hybrids solution on a quartz glass substrate and then heating the samples at 80 °C for 12 h. Finally, white LEDs were constructed by coupling the films with GaN chip.

2.3. Characterization techniques

The microstructure of all the samples were carried out on a FEI Tecnai F20 transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) which was operated at an acceleration voltage of 200 kV. The functional groups on the surface of the LCDs and Ag-LCDs hybrids were detected by the Fourier transform infrared (FTIR), in which the all samples was ground with KBr power and measured using a Bruke Equinox 55 FTIR spectrometer from 500 to 4000 cm^{-1}. Meanwhile, X-ray photoelectron spectroscopy (XPS) analysis was collected using an Axi Ultra DLD spectrometer with monochromatic Al Ka as the excitation source. The UV–vis absorption spectra were recorded with a UV-2450 spectrometer, in which the LCDs and Ag-LCDs were dissolved in ethanol and Ag NPs was dispersed in water. The fluorescence spectra were conducted on a Horiba Jobin Yvon Fluromax-4P spectrophotometer. Time resolved PL lifetime measurements were performed using a time-correlated single-photon counting (TCSPC) lifetime spectroscopy system with a picosecond-pulsed diode laser (EPL-400 nm) as the single wavelength excitation light source. Optical properties such as color rendering index (CRI), color coordinates (CIE), correlated color temperature (CCT) and LE were evaluated employing an integrating sphere (PMS-50, Everfine, China) under a forward current of 20 mA.

3. Results and discussion

3.1. Synthesis and characterization of CDs and Ag-LCDs hybrids

Fig. 2a shows the TEM image of as-synthesized Ag NPs and their size distribution (inset in Fig. 2a), indicating that the Ag NPs are uniformly distributed and the average size of Ag NPs is 15 nm. As depicted in the Fig. 2b, the lattice spacing of 0.236 nm is

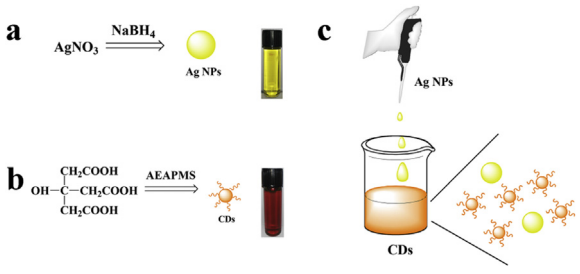

Fig. 1. Schematic of synthesis for the (a), Ag NPs (b), LCDs (b) and (c), Ag-LCDs hybrids.