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Regular Article

Red carbon dots-based phosphors for white light-emitting diodes with color rendering index of 92

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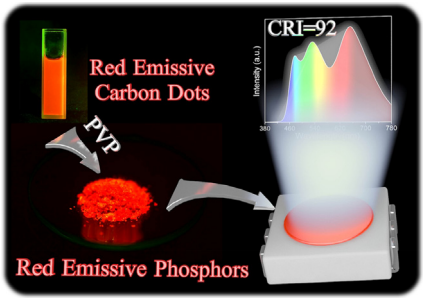
GRAPHICAL ABSTRACT



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ABSTRACT

Exploration of solid-state efficient red emissive carbon dots (CDs) phosphors is strongly desired for the development of high performance CDs-based white light-emitting diodes (WLEDs). In this work, enhanced red emissive CDs-based phosphors with photoluminescence quantum yields (PLQYs) of 25% were prepared by embedding red emissive CDs (PLQYs of 23%) into polyvinyl pyrrolidone (PVP). Because of the protection of PVP, the phosphors could preserve strong luminescence under long-term UV excitation or being mixed with conventional packaging materials. By applying the red emissive phosphors as the color conversion layer, WLEDs with high color rendering index of 92 and color coordinate of (0.33, 0.33) are fabricated.

1. Introduction

White light-emitting diodes (WLEDs) indicate a promising future in replacing the traditional lighting sources, since they are long-lived, eco-friendly and energy-saving [1–4]. Currently, the most common path of manufacturing the WLEDs is based on phosphors and the blue light-emitting InGaN chip [5]. The phosphors are used as color conversion layer to convert the blue emission of the InGaN chip into other emission color, and then the residual non-absorbed blue light and emission from phosphors mix to form white light [6]. Thereby, phosphors, as a significant part of WLEDs, play a pivotal role in determining the performance of WLEDs, such as color rendering index (CRI), correlated color temperature (CCT), Commission Internationale de l'Eclairage (CIE) chromaticity coordinate, luminous efficiency, and so forth [7–9]. At present, commercial phosphors are based on the nonrenewable rare-earth materials, while the exploitation of them would often cause the concerns of environmental destruction [10]. Semiconductor quantum dots (QDs) were proposed to be potential alternative as color

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conversion layer for fabricating WLEDs in the past decade, but the high-performance QDs are often composed of heavy metal elements, such as Cd and Pb, leading to toxicity concerns [11–13]. Perovskite QDs, as an emerging luminescent material, are also expected to be applied for WLEDs. However, their photoluminescent (PL) property could be seriously quenched due to the anion-exchange reaction when being exposed in the air, which restricts their applications as phosphors [14]. Therefore, exploring alternative luminescent materials is an important research avenue to promote the development of LEDs [15,16].

Carbon dots (CDs), an emerging class of carbon-based luminescent nanomaterials, have drawn more and more attention in recent years owing to their outstanding properties, such as chemical stability [17–19], biocompatibility [20–22], photostability [23–26], low toxicity [27–30] and so forth. Because of those distinct merits, CDs could be applied in extensive fields, such as drug delivery, solar cell, optoelectronic devices, bioimaging, and so on [31–44]. Besides, CDs have shown potential to be as a color conversion layer for WLEDs due to their strong luminescence [45]. However, efficient CDs-based phosphors are difficult to achieve, which could be understood in terms of the aggregation-induced luminescence quenching of CDs in the aggregated state [46]. To overcome this problem, several suitable matrices are utilized to ensure the monodispersity of CDs in the solid state, resulting in highly luminescent solid-state materials. For instance, Rogach et al. embedded CDs into polymethylmethacrylate to form luminescent phosphors, and combined the phosphors with ultraviolet (UV) chips to fabricate LEDs [37]. Similarly, in our previous work, CDs were dispersed on the surface of starch, ensuring the monodispersity of CDs and therewith the strong PL emission, which could be used as the color conversion layer for cool WLEDs with CCT of 9892 K [45]. Despite the successes in fabricating LEDs, these approaches still own several limitations for realizing practical illumination. Ideal WLEDs-based illumination source should be based on blue-emitting InGaN chips instead of ultraviolet light to avoid the harm of UV light to the human health [9]. Meanwhile, owing to the lack of efficient red emissive CDs-based phosphors, current CDs-based WLEDs possess low CRI and high CCT, which is not favorable to present the true apparent color [47]. Consequently, it is of great scientific interest and value to develop more efficient routes to prepare CDs-based phosphors for high performance WLEDs with high CRI.

In this work, we prepared red emissive CDs-based phosphors through embedding red emissive CDs (r-CDs) into polyvinyl pyrrolidone (PVP). The as-prepared r-CDs@PVP phosphors exhibit a red emission located at 648 nm and high photoluminescence quantum yields (PLQYs) of 25% under 532 nm excitation, which could be ascribed to the plentiful electron-acceptor group (C═O) of PVP. Additionally, green emissive phosphors based on green emissive CDs (g-CDs) were synthesized [45], which possess strong PL emission centered at 532 nm with PLQYs of 36% under 450 nm light. These CDs-based phosphors exhibit good photostability and structural stability. Based on these advantages, these two phosphors were deposited successively on the InGaN chip of LEDs in order of decreasing PL emission wavelength. In the WLEDs prototype, blue emission (450 nm) of InGaN chip first excite the g-CDs@starch phosphors to emit green light (532 nm), and then r-CDs@PVP phosphors are excited to generate red light, leading to a broad spectrum emission and thereby achieving WLEDs with high CRI of 92 (Fig. 1).

2. Results and discussion

Experimentally, g-CDs are prepared from citric acid and urea by the microwave-assisted heating method [45]. Under sunlight, the diluted solution of g-CDs presents primrose yellow, indicating a strong absorbance of blue light, which is further confirmed by UV–vis absorption spectrum (Fig. S1a). Under 450 nm excitation, g-CDs solution shows strong green emission located at 532 nm (Fig. S1a and b). As shown in Fig. S1c, high resolution transmission electron microscopy (HRTEM) shows that the lattice spacing of g-CDs is 0.21 nm, consistent with the (1 0 0) lattice planes of graphite [32].

To obtain r-CDs, the reaction between citric acid and urea is performed in the solvothermal method as described in MATERIALS AND METHODS. The as-prepared r-CDs are dissolved in dimethylsulfoxide (DMSO), which possesses an obvious absorption in the range of green light (Fig. 2a). Meaningfully, r-CDs presents strong red emission under green light (532 nm) excitation (Fig. 2b), where the electron-acceptor group (S═O) of DMSO is capable of modifying the surface of the r-CDs, thereby influencing the optical band-gap and promoting electron transitions [48]. Furthermore, PLQYs of r-CDs DMSO solution is measured to be 23% under 532 nm excitation. TEM and HRTEM images present monodisperse r-CDs with an average diameter of 3.4 nm and lattice spacing of 0.21 nm, consisting with the (1 0 0) crystallographic facet of graphite (Figs. 2c and S2) [49–52].

To obtain solid-state luminescent materials, these CDs should be dispersed onto matrix to avoid the aggregation-induced

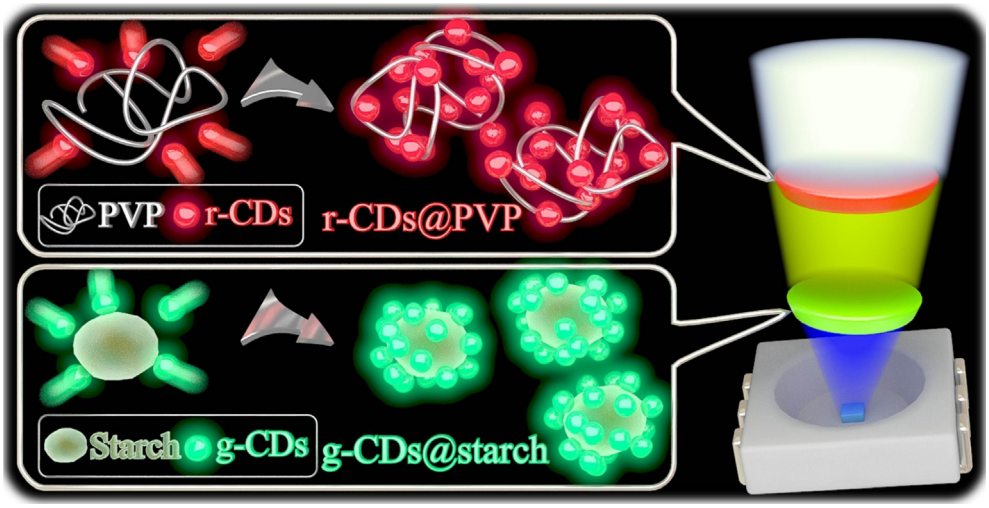

Fig. 1. Schematics of preparation of CDs-based phosphors for WLEDs.