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Towards efficient and stable multi-color carbon nanoparticle phosphors: synergy between inner polar groups and outer silica matrix

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ABSTRACT Nanocarbon as an eco-friendly and abundant material has strong multi-color fluorescence, which makes it a promising candidate for healthy lighting and display. However, the low fluorescence efficiency and poor stability of multi-color carbon nanoparticle (CNP) phosphors are main hurdles that hinder their applications. This work demonstrated efficient and stable multi-color CNP phosphors through synergy between inner polar groups and outer silica matrix. The polar groups in polyethylene glycol (PEG) 6,000 are favor of high fluorescence of the CNP phosphors, and the low melting point (64°C) of PEG 6,000 helps to improve the thermal stability of the phosphors, while the silica matrix provides protection to the phosphors. Based on this design, blue, green, yellow and red CNP phosphors with photoluminescence quantum yield of 53.1%, 47.4%, 43.8% and 42.3% have been achieved, all of which are the best values in ever reported multi-color CNP phosphors. Furthermore, the fluorescence of the CNP phosphors keeps almost unchanged at 100°C and degrades little in one month, indicating their good thermal tolerance and temporal stability. In addition, multicolor devices including white light-emitting devices (LEDs) have been realized by coating the CNP phosphors onto UV chips. The luminous efficiency, correlated color temperature, Commission Internationale de L'Eclairage and color rendering index of the white LED can reach 12 lm W⁻¹, 6,107 K, (0.32, 0.33) and 89, respectively, indicating the potential applications of the CNP phosphors in lighting and display.

Keywords: carbon nanoparticle, phosphor, multi-color, lightemitting devices

INTRODUCTION

Carbon, as one of the most abundant materials on the earth, shows strong multi-color fluorescence once it is tailored into nanoscale size [1-5]. Fluorescent carbon nanoparticles (CNPs) have some distinctive merits, such as high efficiency [6,7], low-cost [8,9], excitation-dependent emission [10-13], low toxicity [14-16], unique biological compatibility [17-20], etc. CNPs have been investigated extensively because of these features, and they have potential applications in various fields including labeling [3,21-24], light-emitting devices (LEDs) [25-27], photocatalysis [28,29], fluorescent ink [30-33], and so on. CNPs, as a class of carbon-based nanomaterials, have been considered a promising candidate as phosphors for LEDs for the possible replacement of limited reversed rare earth elements in the future. However, the fluorescence of CNPs usually is quenched in solid state form, which is usually called aggregation induced quenching, and the quenching hinders their application as phosphors in LEDs greatly [34,35]. For lighting and display, it is important to develop multi-color emission CNP phosphors. Several studies have demonstrated multi-color emission solid-state CNPs by incorporating CNPs into poly(vinyl alcohol) (PVA), polyhedral oligometric silsesquioxane and silica matrix. For example, Tian et al. [36] reported multi-color CNP phosphors with photoluminescence (PL) quantum yield (QY) of 30%-40% by incorporating CNPs into silica network via microwaveassisted method. Feng et al. [37] achieved multi-color

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CNP phosphors by manipulating the supramolecular cross-link degree of CNPs in PVA. Shao et al. [38] reported self-quenching-resistant solid-state fluorescent polymer carbon dots with multi-color emission via modulating the concentration of the carbon dots. However, the PLQY of the multi-color CNP phosphors is still below expectation for high performance LEDs. Additionally, the thermal stability and durability of the CNP phosphors is still poor, and the fluorescence of the CNP phosphors (especially red emission CNP phosphors) degrades significantly after several days. These issues of multi-color CNP phosphors will impede their applications in lighting and displaying. Hence, it is of great importance and significance to develop a strategy that can be used to develop efficient and stable multi-color CNP phosphors, which will take a giant step towards the application of CNPs as phosphors in LEDs.

It has been verified that CNPs prepared by different methods show emission behavior in the presence of polar groups, while the fluorescence will be quenched in other cases [39]. For example, CNPs show strong emission when they are dissolved in water or alcohol due to the presence of polar -OH groups. So if a polar group-rich environment and protection layer can be provided for CNPs in solid state, the PLQY and stability of the CNPs will be increased greatly. In this work, by using the synergy between the inner polar groups and outer silica matrix, efficient and stable multi-color CNP phosphors have been prepared. Based on this design concept, polyethylene glycol (PEG) 6000 was used as polar group supplier for CNPs to form fluorescent CNP-PEG cores. Considering that the melting point of PEG 6,000 is about 64°C, and heat will be absorbed by the melting process of PEG 6,000 when the surrounding temperature exceeds 64°C, and this is favor to the thermal stability of the CNP phosphors. Silica matrix generated from tetraethyl orthosilicate (TEOs) was used to immobilize PEG 6,000 soft segments in solid state to form CNP-PEG@SiO₂ phosphors. As a result, the PEG 6,000 and silica matrix work together for multi-color CNP-based phosphors with high fluorescence and stability resulting from the synergistic effect of the polar groups and silica matrix. With the synergy between inner polar groups and outer silica matrix, the PLQY of the CNP-PEG@SiO₂ phosphors including blue, green, yellow and red can reach 53.1%, 47.4%, 43.8% and 42.3%, all of which are the highest values ever reported for multi-color CNP phosphors to the best of our knowledge. Furthermore, the fluorescence of the CNP-PEG@SiO₂ phosphors degrades little when the temperature reaches 100°C or after storage in ambient environment for over one month. Multi-color LEDs have been realized by coating the CNP-PEG@SiO₂ phosphors onto UV chips, and white LED with luminous efficiency, Commission Internationale de L'Eclairage (CIE), color rendering index (CRI) and correlated color temperature (CCT) of 12 lm W⁻¹, (0.32, 0.33), 89 and 6,107 K has been achieved, indicating the potential applications of the CNP phosphors in lighting and displaying.

EXPERIMENTAL SECTION

Materials: The reagents used in this experiments, including citric acid (purity>99.5%), ethylenediamine (purity>99%), urea (purity>99%), phthalic anhydride (purity>99.5%), *o*-phenylenediamine (purity>99.5%) and dopamine (purity>98%), were purchased from Aladdin and used directly without further purification.

Synthesis of blue CNPs (bCNPs): 0.84 g citric acid and 1,072 μ L ethyenediamine were dissoloved in 20 mL distilled water. Then the mixture was transferred to an autoclave followed by heating for 6 h at 180°C. After the reaction cooled to room temperature naturally, the product was centrifuged at 5,000 rpm for 20 min to obtain bCNPs, and the resulting solution was used for further applications.

Synthesis of green CNPs (gCNPs): 1 g critic acid and 1 g urea were added into 5 mL deionized water and stirred for 5 min to form a transparent solution. After that, the solution was transferred to a 750 W microwave oven for 5 min. In this process, the solution changed from colorless to brown and finally to dark-brown clustered solid. The solid was dissolved into ethanol to form gCNPs.

Synthesis of yellow CNPs (yCNPs): Firstly, 166 mg phthalic anhydride and 216 mg *o*-phenylenediamine were dissolved in 10 mL dimethylformamide, and then the solution was transferred to an autoclave followed by heating for 8 hours at 200°C. Finally, the reactor was cooled to room temperature naturally; the obtained yCNPs were dissolved into ethanol and the solution was centrifuged (10,000 rpm) for 10 min twice to wash off impurities.

Synthesis of red CNPs (rCNPs): 184 mg dopamine and 108 mg *o*-phenylenediamine were dissolved in 10 mL distilled water, and then the solution was transferred to an autoclave followed by heating for 8 h at 200°C. Finally, the supernatant was discarded, the reactor was soaked with ethanol to obtain rCNPs, and then the solution was centrifuged at 10,000 rpm for 10 min twice to wash off impurities.

Synthesis of multi-color CNP-PEG@SiO₂ phosphors:

0.1 mL bCNP solution, 0.1 g gCNP solid, 1 mL yCNP solution, and 1 mL rCNP solution were dispersed into 20 mL ethanol solution. Then, 1 g PEG 6,000, 2 mL TEOs and 1 mL ammonium were added into the ethanol solution followed by stirring for 5 h at room temperature. Finally, the solution was centrifuged at 8,000 rpm for 5 min to obtain the precipitates which were then put into an oven and heated for 5 h to obtain multi-color CNP-PEG@SiO₂ phosphors.

Application in multi-color LEDs: To explore the applications of the CNP phosphors in multi-color LEDs, the phosphors were coated onto UV chips whose emission are centered at around 365 nm, and the UV chips were purchased from Shenzhen Mingto Photoelectric technology Co. Ltd. For fabricating LEDs, polydimethylsiloxane (PDMS) was premixed with the multicolor CNP-PEG@SiO₂ phosphors, and then the PDMS with phosphors was dropped onto the UV chips. Finally, the as-prepared multi-color LEDs were placed into an oven at 60°C for 6 h. For fabricating white LED, PDMS was premixed with bCNP-PEG@SiO₂, gCNP-PEG@SiO₂ and rCNP-PEG@SiO₂ phosphors, respectively. The PDMS with rCNP-PEG@SiO₂ phosphors was dropped onto the UV chip and the chip was put into an oven at 60°C for 6 h. The PDMS with gCNP-PEG@SiO₂ phosphors and the PDMS with bCNP-PEG@SiO₂ phosphors were sequentially dropped onto the UV chip following the same procedure as above.

Characterizations: The morphologies of the samples were characterized using JEM-2010 transmission electron microscopy (TEM) and JSM-6700F scanning electron microscopy (SEM). The structural properties of the samples were characterized using X'pert Pro X-ray diffractometer (XRD). The composition and binding state of the samples were assessed using Thermo ESCALAB-250 X-ray photoelectron spectroscopy (XPS). The radicals on the CNPs were characterized using a Bruker VERTEX-70 Fourier transform infrared (FTIR) spectrometer. The fluorescence spectra of the CNPs were recorded by a Hitachi F-7000 spectrophotometer. The PLQY of the samples were measured in a calibrated integrating sphere in FLS920 spectrometer. The transient fluorescence lifetime of the samples were recorded in a FLS-920 fluorescence spectrometer. The luminous efficiency of the fabricated white LED was recorded by radiometer PM6612L. The preservation time of the carbon dot phosphors at each temperature is 30 min, which is conducted at a hot plate. Thermogravimetric analysis (TGA) was performed by using a NETZSCH STA 449C analyzer.

RESULTS AND DISCUSSION

The blue, green, yellow and red emission CNPs were prepared according to previous reports, [1,21,40,41] and the CNPs show bright emission in alcohol solution, as shown in Fig. S1. In general, most silica-based CNPs were prepared through Stober method, in which CNPs were subjected to surface treatment with stabilizers to avoid phase separation [42-44]. In addition, it has been reported that the precipitates centrifuged from reacting mixture of CNPs, TEOs, ammonia and water/ethanol show no obvious fluorescence, which means that silica does not physically encapsulate CNPs [45]. Besides, it has been reported that CNPs show strong emission behavior under polar group, and the fluorescence mechanism can be explained by molecular fluorescence theory [39]. The molecules fluorescence is polarity dependent [46,47], and CNPs have low-lying and closely spaced n and π orbitals in HOMO level due to the presence of lone pair electrons. The π - π^* transition is symmetry-allowed while n- π^* transition is symmetry-forbidden, and thus the PLQY of π - π^* transition is higher than that of n- π^* transition. Once the polarity of the environment increases, n electrons with higher polarity are more stable than π ones through the interaction of dipole-dipole interaction or hydrogen bonding. As a result, n orbital shifts to a lower level and more π orbital electrons leave on the HOMO level, promoting π - π * transition, so that the synthesized CNP-PEG@SiO₂ phosphors can maintain relatively high PLQY. Based on this design concept, PEG 6,000 with polar groups and strong positive charges in alcohol solution (Fig. S2) was introduced to this system as the supplier of polar groups to achieve efficient multi-color CNP-based phosphors, and silica matrix was used to immobilize PEG chains and protect the phosphors. For illustrative purposes, bCNPs were used as an example to explore the optimal experiment conditions. The mixture (ethanol, TEOs, ammonium, PEG 6,000 and bCNPs) stirred for different hours at room temperature are shown in Fig. 1a. With the increase of reaction time, the solution changes from clear to turbid gradually, indicating the CNP-PEG@SiO₂ phosphors have been formed. The mixture processed with different stirring durations was centrifuged and then the precipitates were dried in an oven, and white powders were obtained, as shown in Fig. 1b. The images shown in the bottom of Fig. 1b are the fluorescence images of the phosphors under illumination of the 365 nm line of a xenon lamp, and bright blue fluorescence can be observed from these phosphors, indicating blue emission CNP-PEG have been encapsulated by silica matrix. The PL spectra of the phosphors are



Figure 1 (a) The images of the mixture of bCNPs, ethanol, TEOs, ammonium, and PEG 6,000 stirred for different hours. (b) The bCNP-PEG@SiO₂ phosphors under indoor lighting (up) and UV lighting (bottom) conditions. (c) The fluorescence spectra of the phosphors under different stirring hours. (d) The fluorescence intensity and weight variation of the bCNP-PEG@SiO₂ phosphors *versus* stirring duration.

shown in Fig. 1c. The spectra are peaked at around 440 nm, which are almost the same with those of bCNPs in ethanol solution (Fig. S3). The PL intensity and weight of the phosphors versus stirring time are shown in Fig. 1d. One can see that the PL intensity increases firstly and reaches its maximum when the stirring time is 5 h and then decreases gradually. In this reaction, the amount of CNPs adsorbed to the PEG increases with time and reaches saturation after 5 h, thus causing the PL intensity to increase gradually. The decrease of PL intensities can be attributed to the thickened silica shell with time. Obviously, the weight of the phosphors increases quickly in the first five hour, and it increases slowly after that. The influence of PEG 6,000 and TEOs to PL intensity of bCNP-PEG@SiO₂ has been recorded, as shown in Figs S4, S5. With the increase of PEG 6,000 weight (0.5-2.5 g), the PL intensity increases due to the increase of CNP attachment point; while with the increase of TEOs weight (1-3 mL), the PL intensity increases firstly then decreases. According to the above results, PEG 6,000, TEOs and reaction time of 2.0 g, 2 mL and 5 h are used to prepare multi-color CNP-based phosphors in view of the PL intensity and phosphors yield.

According to the above proposed strategy, the synthesis process of blue, green, yellow and red emission CNP-PEG@SiO₂ phosphors is shown in Fig. 2a, and the images of the prepared phosphors are shown in Fig. S6. The prepared multi-color CNP-PEG@SiO2 phosphors show bright fluorescence under UV illumination, as shown in Fig. 2b. Fig. 2(b1-3, 6) are the pictures of blue, green, yellow and red emission CNP-PEG@SiO2 phosphors, which are prepared by PEG 6,000 adhesion and silica encapsulation from blue, green, yellow and red emission CNPs, and the orange and pink CNP-PEG@SiO₂ phosphors are prepared by mixing yellow and red emission phosphors, blue and red emission phosphors with mass ratio of 1:3, respectively. The corresponding PL spectra of the different emission CNP-PEG@SiO₂ phosphors are shown in Fig. 2c, which cover the entire visible region with wavelength ranging from 400 to 700 nm. The PLQY of the blue emission, green emission, yellow emission, and red emission CNP-PEG@SiO2 phosphors can reach



Figure 2 (a) The synthesis process of the multi-color $CNP-PEG@SiO_2$ phosphors. (b) Images of the multi-color $CNP-based CNP-PEG@SiO_2$ phosphors under the illumination of 365 nm. (c) The corresponding PL spectra of the CNP-PEG@SiO_2 phosphors. (d) The CIE coordinates of the multi-color phosphors, the NTSC area is marked by white triangle. (e) The thermogravimetric analysis spectra of the multi-color phosphors. (f) The PL intensity of the phosphors variation *versus* heating temperature. (g) The PL intensity of the phosphors stored in ambient environment for one month.

53.1%, 47.4%, 43.8% and 42.3%, respectively, all of which are the highest value ever reported for multi-color CNPbased phosphors to our knowledge. The recent reported multi-color CNPs and CNP-based phosphors are summarized in Table 1. The corresponding CIE coordinates of the CNP-PEG@SiO₂ phosphors are shown in Fig. 2d, and the national television system committee (NTSC) area is also marked in the figure with white triangle. The CIE coordinate distributions of the CNP-PEG@SiO₂ phosphors cover most of the NTSC standard CIE coordinates, as shown in Fig. 2d. Stability is an important parameter that determines the performance of phosphors, and the stability of the multi-color CNP-PEG@SiO2 phosphors has been analyzed by TGA, as shown in Fig. 2e. The weight decreases slowly when temperature is lower than 400°C, which can be attributed to evaporation of the adsorbed water. The weight decreases further when the temperature is over 400°C, which indicates the decomposition of the phosphors. It can be concluded that the silica matrix can provide protection and support for the CNPs within the matrix to maintain thermal stability of the CNP-PEG@SiO₂ phosphors. The PL stability of the multi-color CNP-PEG@SiO₂ phosphors has been analyzed by heating the phosphors under different temperatures, as indicated in Fig. 2f. The PL intensity of the blue, green, yellow and red emission phosphors keeps unchanged even when the temperature is increased to 100°C, indicating the good thermal tolerance of the phosphors. Remarkably, the PL intensity of the phosphors changes little when stored in ambient conditions for one month, as shown in Fig. 2g, indicating the good thermal tolerance and temporal stability of the phosphors. We think that the good thermal tolerance and temporal stability of the phosphors comes from the heat preservation effect of the PEG 6,000 and protection of the silica matrix.

The morphology of the bCNP-PEG@SiO₂ is presented in Fig. 3a, uniform and globular microstructures can be observed clearly from the image. Fig. 3b shows the magnified SEM image of the sample, and the size of the blue emission CNP-PEG@SiO₂ is around 500–600 nm. In order to determine the composition of the phosphors, elemental mapping using energy-dispersive X-ray spec-

The summary of the parameters for recent reported main color of the phosphore					
Strategy	Blue	Green	Red	Deferrer	Vaar
	Quantum yield			- Reference	rear
Incorporating CNPs into silica network <i>via</i> micro- wave-assisted method	40%	34%	30%	[36]	2017
Manipulating the supramolecular cross-link degree of CNPs in PVA	4.60%	8.60%	0.50%	[37]	2017
Modulating the concentration of the carbon dots	18.90%	5.50%	8.50%	[38]	2017
Synergy between inner polar groups and outer silica shell	53.10%	47.40%	42.30%	This work	_

Table 1 Summary of the parameters for recent reported multi-color CNP phosphors



Figure 3 (a) SEM image of the bCNP-PEG@SiO₂ phosphors. (b) Magnified SEM image of the bCNP-PEG@SiO₂ phosphors. (c) Elemental mapping of the phosphors. (d) XPS spectra of the phosphors, the inset is the C 1s spectrum, which can be well fitted by three peaks. (e) FTIR spectra of the PEG 6,000 and bCNP-PEG@SiO₂ phosphors. (f) XRD pattern of the bCNP-PEG@SiO₂ phosphors, the inset is the XRD patterns of the gCNP-PEG@SiO₂ phosphors, yCNP-PEG@SiO₂ phosphors and rCNP-PEG@SiO₂ phosphors.

troscopy (EDX) was recorded, as shown in Fig. 3c. The elements of C, O and Si can be observed from the figure, and the distribution of C element matches well with that of O and Si, indicating the CNPs are encapsulated by silica matrix. The morphology and elemental mapping of the gCNP-PEG@SiO₂, yCNP-PEG@SiO₂ and rCNP-PEG@SiO₂ phosphors are shown in Fig. S7. XPS was used to investigate the binding states of the bCNP-PEG@SiO₂ phosphors, as shown in Fig. 3d. Four peaks can be observed in the survey spectrum, and they can be attributed to Si 2p (103.6 eV), Si 2s (154.5 eV), C 1s (285 eV) and O 1s (531.1eV), respectively. The carbon peak shown in the inset of Fig. 3d can be well fitted by three peaks, which correspond to aliphatic carbon, oxygenated carbon, and nitrous carbon on the CNPs, respectively. The XPS spectra of green emission, yellow emission and red emission phosphors are shown in Fig. S8. To study the formation mechanism of the bCNP-PEG@SiO₂ structure, FTIR spectra of the CNP-PEG@SiO₂ and PEG 6,000 were recorded, as shown in Fig. 3e. The FTIR spectra of the green emission, yellow emission, and red emission CNP-PEG@SiO₂ phosphors are shown in Fig. S9. In the FTIR spectrum of PEG 6,000, the peaks centered at around 3,493 and 2,889 cm⁻¹ can be attributed to the stretching vibration of -OH and -CH₂-, respectively. The peaks at 1,468 and 1,343 cm⁻¹ belong to the bending vibration of -CH₂-, and the asymmetrical and symmetrical stretching vibration of -C-O-C- are centered at 1,243 and $1,103 \text{ cm}^{-1}$. The peaks centered at 961 and 842 cm⁻¹ stem from the in-plane bending vibration of -C-O-C- and -CH₂-CH₂-OH, respectively. In the FTIR spectrum of the bCNP-PEG@SiO₂, the peak at 454 and 1,075 cm⁻¹ can

be attributed to vibration absorption of -Si-O-Si-, indicating the formation of silica matrix. In addition, the peaks of the PEG 6,000 can also be found in the FTIR spectrum of the bCNP-PEG@SiO₂, but their intensity decreases greatly compared with those of the PEG 6,000. The decreased intensity of the PEG 6,000 can be understood as follows: In the bCNP-PEG@SiO2, CNPs were adsorbed by PEG 6,000 molecular chains and then the PEG 6,000 molecular chains were encapsulated by silica matrix. As a result, the molecular chains of the PEG 6,000 will be immobilized into the silica gridding, leading to the decrease of vibration intensity due to the restriction of the silica matrix. The merits of the CNP-PEG@SiO₂ structure are listed below: Firstly, the CNPs can maintain higher PLQY due to the presence of polar groups in the PEG 6,000; Secondly, the melting point of the PEG 6,000 is about 64°C, so when the ambient temperature is approaching 64°C much heat will be absorbed by the PEG 6,000 to support its melting process, which is favorable for the thermal tolerance of the phosphors. Thirdly, the silica matrix can help to maintain the structure in solid state form even when the surrounding temperature is higher than 64°C. XRD pattern of the bCNP-PEG@SiO₂ phosphors is shown in Fig. 3f, and only one peak centered at around 23° can be observed from the pattern, which can be attributed to the diffraction of amorphous silica. The diffraction patterns of the green emission, yellow emission, and red emission CNP-PEG@SiO2 phosphors are shown in the inset of Fig. 3f. From the above data, one can conclude that the CNPs are adsorbed to the PEG 6,000 to form CNP-PEG fluorescent composites, and the composites are encapsulated by silica to form CNP-PEG@SiO2 phosphors.

Fig. 4a shows the TEM image of the CNP-PEG@SiO₂ phosphors. It is evidenced from the image that multiple CNPs with diameter ranging from 5 to 10 nm were encapsulated by silica. Some corrugations located around the CNPs can be observed clearly in the high-resolution TEM image, as shown in Fig. 4b, and the corrugation parts are PEG 6,000 that adhere to the CNPs through electrostatic adsorption.

The interlayer spacing of 0.21 nm can be observed from the inset of Fig. 4b, which corresponds to the d-spacing of the graphene (100) planes. According the above results, the growth mechanism of the CNP-PEG@SiO₂ is schematically illustrated in Fig. 4c. The CNPs have negative charges when they are dissolved in ethanol (Fig. S10), while PEG 6,000 has positive charges in alcohol solution (Fig. S2). As a result, CNPs and PEG 6,000 will stick together *via* electrostatic adsorption, then the PEG 6,000



Figure 4 (a) TEM image of the CNP-PEG@SiO₂ phosphors. (b) High resolution TEM image of the CNP-PEG@SiO₂ phosphors. (c) Schematic illustration of the formation process of the CNP-PEG@SiO₂ phosphors.

react with TEOs to form silica matrix encapsulated CNP-PEG nanocomposites in ammonium ambient.

To understand the fluorescence mechanisms of the CNP-PEG@SiO₂ phosphors better, the PL dynamics spectra of the CNPs ethanol solution and CNP-PEG@-SiO₂ phosphors have been recorded, as shown in Fig, S11. Fig, S11a and b are the decay times of the CNPs ethanol solution and CNP-PEG@SiO₂ phosphors, which show the same trend in shape. The PL decay times were fitted by using single-exponential decay kinetics, and the decay times of the blue emission, green emission, yellow emission, and red emission CNPs in ethanol are 10.46, 11.79, 3.35 and 3.49 ns, as marked in Fig. S11a1-a4, and the decay times are 10.21, 11.58, 3.06 and 2.51 ns in CNP-PEG@SiO₂ phosphors, as marked in Fig. S11b1-b4. Obviously, the decay times of the CNPs ethanol solution and CNP-PEG@SiO₂ phosphors are almost the same, revealing that the adhesion of PEG 6,000 and encapsulation of silica has not altered the carrier recombination dynamics of the CNPs greatly [48].

To test whether the multi-color CNP-PEG@SiO₂ phosphors can be employed as phosphors for LEDs, the multi-color CNP-based phosphors have been mixed with PDMS, and the mixture was dropped onto UV chips with emission centered at 365 nm, then the chips were heated in an oven at 60°C for 6 h to cure the PDMS. Fig. 5 shows the emission images and spectra of the LEDs under the driving currents of 30 mA. By coating multi-color CNP-PEG@SiO₂ phosphors onto the UV chips, bright blue, green, yellow, red and white light emission LEDs can be fabricated, as shown in Fig. 5a. The spectra of the LEDs cover from 400 to 700 nm. Besides, by coating the red emission, green emission, and blue emission CNP-



400 450 500 550 600 650 700 Wavelength (nm)

Figure 5 (a) Emission photographs of the LEDs employing the multicolor CNP-PEG@SiO₂ phosphors as fluorescence phosphors. (b) The corresponding fluorescence spectra of the LEDs. (c) The corresponding CIE coordinates of the LEDs.

PEG@SiO₂ phosphors successively onto the UV chips, white LEDs with CIE of (0.32, 0.33) can be achieved, which is very close to standard white emission (0.33, 0.33), and the CRI and CCT can reach 89 and 6,107 K. Thanks to the abundance and eco-friendly properties of carbon, the multi-color CNP-based phosphors may find potential applications as fluorescent phosphors in lighting and display in the future.

CONCLUSIONS

In summary, efficient and stable multi-color CNP-based phosphors through synergy between inner polar groups and outer silica matrix have been demonstrated. The PLQY of the blue, green, yellow and red CNP-PEG@SiO₂ phosphors can reach 53.1%, 47.4%, 43.8% and 42.3%, all of which are the highest value ever reported for multicolor CNP-based phosphors to the best of our knowledge. Additionally, the fluorescence of the CNPs degrades little when heated to 100°C or stored in ambient environment for one month, indicating the good thermal tolerance and temporal stability of the CNP phosphors. The high PLQY of the CNP phosphors can be attributed to the polar groups of the PEG 6,000, while the good stability to heat preservation effect of the PEG 6000 and the protection of the silica matrix. LEDs have been fabricated by coating the CNP phosphors onto UV chips, and bright blue, green, yellow, and red LEDs have been realized. Notably, by mixing the composition of the blue, green, and red CNP phosphors, white emission LEDs have been fabricated, and the CIE of the LEDs can reach (0.32, 0.33), which is very close to the standard white emission. The CRI and CCT of the white LEDs are 89 and 6,107 K, indicating the potential application of the CNP phosphors in lighting and display. Considering the abundance and eco-friendly properties of carbon, the results reported in this paper may promise the potential applications of CNPs in healthy lighting and display.

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Author contributions Liu K designed the experiment, discussed the results and wrote the manuscript. Zhou R and Liang Y prepared the carbon dots, Guo C polished the language, Xu Z contributed to the TEM measurements of the samples. Li L discussed the results. Shan C conceived the idea and discussed the results. Shen D supported the program.

Conflict of interest The authors declare no conflict of interest.

Supplementary information Supporting data are available in the online version of the paper.



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高效稳定的多色碳纳米颗粒荧光粉:内层极性官能团与外层二氧化硅的协同作用

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摘要 纳米碳作为一种资源丰富的环境友好型材料,会产生明亮的多色荧光,成为一种在健康照明与显示领域有前景的材料.然而多色碳 纳米粒子荧光粉的荧光效率和稳定性仍然低于预期,这极大地限制了碳纳米粒子的应用.本工作通过内层极性官能团与外层二氧化硅的 协同作用,制备了高效稳定的多色碳纳米颗粒荧光粉.聚乙二醇6000中的官能团有利于碳纳米粒子的发光,其较低的熔点(64°C)提升了碳 纳米粒子的热稳定性,而外层的二氧化硅对荧光粉提供了保护作用.基于这个设计,制备出了量子效率为53.1%,47.4%,43.8%以及42.3%的 蓝光、绿光、黄光和红光碳纳米粒子荧光粉,量子效率均为已报道的多色碳纳米粒子荧光粉的最高值.所制备的碳纳米粒子荧光粉展现 了良好的热稳定性和时间稳定性,其荧光在100°C和一个月后仍能保持不变.将所制备的碳纳米粒子荧光粉涂覆到紫外芯片上,实现了包 括白光在内的多色发光器件.其中,白光器件的流明效率为12 lm W⁻¹,色温,色坐标和显色指数分别为6107 K,(0.32,0.33)和89,表明碳纳米 粒子荧光粉在照明与显示领域有潜在的应用前景.