Nitrogen-induced shift of photoluminescence from green to blue emission for xylose-derived carbon dots

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Abstract  
The discovery of carbon dots opens a new avenue to the applications of nanomaterials in biosensing and bioimaging. In this work, we develop simple methods to prepare carbon nanoparticles from xylose and to tune the photoluminescence (PL) characteristics of the xylose-derived carbon nanoparticles via the combination of three different processes: hydrothermal carbonization (HTC), annealing at 850 °C and laser ablation (LA) in a NH₄OH solution. The HTC-synthesized carbon dots (CDs) exhibit green emission under the 365 nm UV excitation, the annealing of the HTC-synthesized CDs leads to complete loss of the PL characteristics, and the LA processing of the annealed carbon nanoparticles recovers the PL characteristics with blue shift in comparison to the HTC-synthesized CDs under the same UV excitation. The PL characteristics of the HTC-CDs and the LA-CDs are dependent on the π-π* transition of C-containing surface-functional groups and π-π* and n-π* transitions of N-containing surface-functional groups, respectively, which are responsible for the difference in the PL characteristics between the HTC-synthesized CDs and the LA-processed CDs. The approaches demonstrated in this work provide a viable method to introduce and tune surface-functional groups on the surface of carbon nanoparticles.

1. Introduction

Multicolor photoluminescent (PL) materials have attracted great interest because of many potential applications [1]. Many multicolor PL materials, including semiconductor quantum dots and fluorescent organic dyes usually contain heavy metals of high toxicity, which can cause severe environmental concerns. Also, the poor water solubility and complicated preparation processes have limited their practical applications. All of these has stimulated the interest in the synthesis of photoluminescent carbon-based materials like carbon dots [2], which are free from heavy-metals and of low toxicity [3–7], for the applications in nanotechnology, biosensing, bioimaging, etc [2].

To date, various methods have been developed to synthesize CDs from different precursors, including pyrolysis, electrochemical synthesis, microwave-assisted synthesis, and hydrothermal treatment and laser-ablation [8–12], and the precursors can vary from simple components or chemical mixtures to biomass. To improve the water solubility and/or luminescence properties of CDs, some methods likely involve a tedious purifying process, the use of a strong acid and the use of surface passivating agents, which can produce many hazardous byproducts. Hydrothermal carbonization (HTC) is a ‘green’, facile and effective synthesis approach to produce photoluminescent CDs from natural products, including orange juice [13], soy milk [14] and Bombyx mori silk [15]. Laser ablation in liquid (LAL) is an effective technique to produce nanomaterials with various functionalized nanostructures [16–18], and the laser ablation of a carbon-based material immersed in water or another solvent can lead to the formation of carbon-based nanoparticles [19–21].
The chemical structures of CDs determine their PL characteristics. There are two competing mechanisms controlling the PL characteristics of CDs. The first one is the band gap associated with sp² hybridized nanodomains, which is dependent on the size of carbon nanoparticles and determines intrinsic emission. The distribution of the sp² domain sizes plays an important role in the emission of CDs [22]. The other one is the surface state determined by surface-functional groups, and the associated emission is referred to as extrinsic emission [22, 23]. Other factors, which can affect the PL behavior of CDs, include the conjugated π-domains determined by carbon-core structures, molecule states, carbon-core states, the crosslink-enhanced emission, zigzag/armchair edges and carbon vacancy [24, 25]. Currently, there are few studies focusing on the CDs derived from the same precursors, which exhibit different PL characteristics with and without surface-functional groups.

Most CDs are generally heterogeneous and multidispersed, and exhibit multicolor emission under the excitation of single wavelength [26]. It is very difficult, if not impossible, to reveal the effects of chemical structures and surface-functional groups on the PL characteristics of CDs, which can limit the applications of CDs. It is known that the morphology and size of CDs produced from the HTC process are dependent on the concentration of precursors, reaction time and temperature [27], and the post processing at high temperatures can alter the chemical structures of carbon nanomaterials. For example, Lingam et al [28] reported the effects of annealing and passivation on the edge-states of graphene quantum dots and found the decrease of the PL intensity of the graphene quantum dots from the edge state with increasing annealing temperature in vacuum (~1 mbar). They suggested that the edge passivation due to annealing led to the quenching of the PL signal.

With the potential applications of CDs, it is of paramount importance to tune the chemical structures and surface-functional groups of CDs with controllable PL characteristics. The purpose of this work is to explore the possibility of synthesizing monodispersed CDs with and without surface-functional groups from xylose and to investigate the PL characteristics of the prepared CDs. Three processes of HTC, high-temperature annealing and laser ablation are used in the synthesis of CDs. The morphology, chemical states of elements and surface functional groups of the prepared CDs are characterized. The mechanisms controlling the PL properties of the prepared CDs are discussed.

2. Experimental details

A solution of ~10 g xylose and 50 ml distilled water was placed in a Teflon-lined autoclave, which was sealed for the HTC processing. The HTC processing was carried out in an oven at 200 °C for 6 h. Following the HTC processing, the power of the oven was turned off, and the Teflon-lined autoclave was cooled to room temperature naturally in the oven. The HTC product formed in the Teflon-lined autoclave was collected by centrifugation at 6000 rpm for 30 min and washed with distilled water several times. The HTC product was then dispersed in DI water sonically and filtrated through a syringe filter with pore size of 450 nm. The resultant filtrate was named as HTC-CDs and stored in an oven.

The annealing of the HTC products was performed in a horizontal quartz tube furnace. For detailed information see the work of Wang et al [29]. Briefly, dried HTC products were annealed at a temperature of 850 °C for 2 h with the flow of argon at 50 SCCM in flow rate. The black carbon powders formed during the annealing were dispersed in deionized water and filtrated with a syringe filter of 450 nm. The resultant filtrate was named as Annealed-CDs and stored in an oven.

Following the process given by Wang et al [29], we performed laser ablation of the Annealed-CDs. For the information of the equipment setup, see the work by Wang et al [29]. Briefly, a circular pellet of ~1.27 cm in diameter, which consisted of ~0.06 g annealed carbon powder and 20 wt% Teflon powder, was prepared. The circular pellet was immersed in a 5 vol% NH₄OH aqueous solution. The pulse width of laser was 1–2 ns, and the repetition rate was 50 Hz. The laser ablation was conducted at 100 mJ p⁻¹ of 532 nm in wavelength for 1 h. After the laser ablation, the suspension was collected and filtered with a syringe filter of 450 nm. The resultant filtrate was exposed to air for the evaporation of NH₄OH, and the final product was dispersed in 4 ml DI water sonically for 1 h under neutral condition. The obtained CDs were named as LA-CDs.

The conversion rates from the HTC-processed carbon particles to the annealed carbon particles and from the annealed carbon particles to LA-processed carbon particles are 80%–90%. The yield of the HTC-processed carbon particles from xylose is 30%–40% after hydrothermal carbonization at 200 °C for 6 h. After high temperature annealing in argon, the yield of the annealed carbon particles is ~50%, and the yield of the LA-processed carbon particles is 70%–80%.

The morphologies and microstructures of the prepared carbon nanoparticles were characterized on a transmission electron microscope (TEM) (Talos F200X), and ImageJ software was used to analyze the particle size of the CDs. The chemical states and structures of elemental components on the CDs were analyzed on a Thermo Scientific K-Alpha x-ray Photoelectron Spectrometer (XPS).
The PL characteristics of the CDs were analyzed on a fluorometer (HORIBA, Fluoromax-4) with a 120 W xenon lamp as the source of excitation light, and the absolute quantum yield (QY) of the CDs was determined on a spectrofluorometer (Horiba Fluoromax-4) with integrating sphere. UV–visible absorption spectra of the CDs were obtained on an UV-visible spectrophotometer (Thermal Scientific Evolution 201). A quartz cubic cell of 1 cm in light-path was used for the measurements of both photoluminescence and UV–vis absorption. Fourier-transform infrared spectroscopy (FT-IR) spectra of the CDs were collected on a Fourier transform infrared instrument (Nicolet iS50, Thermo Scientific) in a wavenumber range of 400 to 4000 cm⁻¹ at a resolution of 4 cm⁻¹. Time-Correlated Single-Photon counting (TCSPC) was used to examine the PL lifetimes of the CDs on a DeltaHub™ with a 393 nm pulsed NanoLED excitation source, and the Horiba Scientific Decay Analysis Software was used to fit the TCSPC curves. All the measurements were performed at room temperature.

3. Results

Figure 1 shows TEM images, SAED (selected area electron diffraction) patterns and lattice profiles of the xylose-derived CDs: (a)–(c) HTC-CDs, (d)–(f) Annealed-CDs, and (g)–(i) LA-CDs. The shape of carbon nanoparticles after the annealing and laser ablation remained almost unchanged, suggesting relatively stable topologies of the HTC-CDs. Both the annealing at high temperature and the laser ablation did not cause any significant change in the topologies of carbon nanoparticles. The SAED patterns embedded in figures 1(a), (d) and (g) exhibit a broad hump and no sharp diffraction peaks appear, suggesting that the carbon nanoparticles derived from xylose are mostly amorphous.

The HRTEM images of some HTC-CDs, Annealed-CDs and LA-CDs are depicted in figures 1(b), (e) and (g). It is evident that there is no lattice profile presented in the HTC-CD, suggesting the amorphous state of the HTC-
CD. Lattice profiles indeed are presented for some Annealed-CDs and LA-CDs, indicating the presence of annealing-induced graphitization of HTC-CDs and possible laser-induced graphitization of carbon nanoparticles. From the lattice profiles, the lattice spacing of the Annealed-CDs was determined to be 0.21 nm (figure 1(e)), corresponding to the (1 1 0) plane of graphite. The lattice spacing of the LA-CDs is 0.31 nm (figure 1(h)), which is larger than the Annealed-CDs. Such a result is likely due to the laser-induced deformation of CDs.

The XRD patterns of the carbon particles are presented in figure S2 in supplementary information, which is available online at stacks.iop.org/NANOX/1/020018/mmedia. The XRD pattern of the HTC-processed carbon particles has a broad peak at 23°, in accord with the HRTEM result. After the annealing and LA processing, both the Annealed and laser-processed carbon particles exhibit a small, broad peak at 43°, suggesting the presence of annealing-induced graphitization of HTC-CDs and possible laser-induced graphitization of carbon nanoparticles. The results are consistent with the HRTEM images in figures 1(e) and (g).

From the TEM images, we used the ImageJ software to analyze the size distribution of the prepared carbon nanoparticles. Figures 1(c), (i) and (d) depicts the histograms of the carbon nanoparticles of the HTC-CDs, Annealed-CDs and LA-CDs, which are presented in a Δ-shape. The histogram of the HTC-CDs is similar to that of the LA-CDs with a long tail, while the histogram of the Annealed-CDs exhibits a long front. Using the histograms, we obtain average particle sizes of 4.72 ± 0.72 nm, 4.40 ± 1.65 nm and 4.23 ± 1.66 nm for the HTC-CDs, Annealed-CDs and LA-CDs, respectively. The LA-CDs have the largest average particle size, and the LA-CDs have the smallest average particle size. Both the annealing at high temperature and the laser ablation led to slight decrease of the average particle size. There is no significant difference in the range of the particle sizes between the HTC-CDs and Annealed-CDs, while the laser ablation increased the range of the particle sizes more than two times of that for the HTC-CDs and Annealed-CDs. The small range of the particle sizes for the HTC-CDs and Annealed-CDs suggests that both the HTC-CDs and Annealed-CDs can be approximated as monodispersed, and the large range of the particle sizes for the LA-CDs reveals that the LA-CDs are multidispersed.

Figures 2(a)–(c) shows the PL spectra of the xylose-derived carbon nanoparticles prepared by the three different processes. Both the HTC-CDs and LA-CDs exhibited strong emission under the excitation of UV-visible light, revealing the broad PL characteristics of the HTC-CDs and LA-CDs. The strongest emission peaks for both the HTC-CDs and LA-CDs are present under the excitation of UV lights of 330, 360 and 390 nm in wavelength. Note that the HTC-CDs exhibited green emission, and the LA-CDs exhibited strong blue emission. There is no emission for the Annealed-CDs under the excitation of UV-visible light. The difference in the emission wavelength for the same group of CDs from different batches (more than five), which were made in a span of more than one year, is within ±3 nm.

According to figure 2(a), exposing the HTC-CDs to UV-visible light in a wavelength range of 300 to 480 nm led to strong fluorescent emissions, suggesting that the PL characteristics of the HTC-CDs is dependent on the excitation wavelength. The maximum emission for the HTC-CDs appears at 466 nm under the excitation of 360 nm, and the corresponding FWHM is 123 nm.

The Annealed-CDs exhibited a significantly different PL spectrum from the HTC-CDs for the excitation wavelength in the range of 250 nm to 600 nm (figure 2(b)). The sharp peaks represent the water Raman scattering [30] instead of the emission from the Annealed CDs. The UV-visible light cannot excite the Annealed CDs to emit photons.

It is interesting to note that the LA-CDs exhibited strong emission under the irradiation of UV-visible light in the wavelength range of 250 to 480 nm (figure 2(c)). The laser ablation of the non-emitted Annealed-CDs led to the recovery of the PL characteristics. The maximum emission of the LA-CDs appeared at 464 nm under the excitation of 390 nm, and the corresponding FWHM is 94 nm. Under the excitation of 360 nm, the emission wavelength of the LA-CDs is 446 nm instead of 466 nm for the HTC-CDs. Such a result reveals that the LA-CDs possess different PL characteristics from the HTC-CDs. The laser ablation of the Annealed-CDs in the 5 vol% NH4OH solution likely introduced surface-functional groups on carbon nanoparticles, resulting in the recovery of the PL characteristics, which are different from the HTC-CDs.

The difference in the PL characteristics among the HTC-CDs, the Annealed-CDs and the LA-CDs can be observed from the optical images embedded in the corresponding figures. The aqueous solution consisting of either HTC-CDs or LA-CDs exhibited light-yellow color (figures 2(a) and (c)) under natural light, and the aqueous solution consisting of Annealed-CDs is transparent (figure 2(b)).

Figure 2(d) shows the UV-Vis spectra of the HTC-CDs, Annealed-CDs and LA-CDs. There are two peaks for the HTC-CDs: one is at 226 nm from the n-π* transition of aromatic carbon rings [2, 14], and the other is at 277 nm from the n-π* transition of carbonyl and other oxygen-containing groups [31].

In contrast to the HTC-CDs, the Annealed-CDs exhibited continuous absorbance in the wavelength range of 200 to 700 nm and a weak peak at 367 nm. Such a result suggests that the Annealed-CDs, as derived from the annealing of HTC-CDs at 850 °C, are likely a metallic, zero-bandgap material [22] with relatively few n-π* transitions.
transition. The annealing of the xylose-derived carbon nanoparticles at high temperature caused the change in the chemical structures/states of the carbon nanoparticles and the loss of PL characteristics.

The LA-CDs exhibited a broad absorption with a peak at 270 nm and a long tail with a small peak at 302 nm. The peak at 270 nm corresponds to aromatic $\pi$ system or isolated sp$^2$-hybridized clusters within the carbon-oxygen matrix [6, 32]. The corresponding intensity of the peak is much smaller than that at 277 nm for the HTC-CDs. The small peak at 302 nm can be ascribed to the complex n-$\pi^*$ transitions of carbonyl and other oxygen and amino groups on the surface of CDs [31, 33]. The differences between the $\pi$-$\pi^*$ and n-$\pi^*$ transitions of the HTC-CDs and the LA-CDs suggest the difference in the surface states as well as surface-functional groups.

The Time-Correlated Single Photon Counting (TCSPC) lifetime measurement was conducted for both the HTC-CDs and LA-CDs under 393 nm irradiation. The emission was recorded at 464, 487, and 474 nm, respectively, which are associated with the wavelengths of the strongest emission for the HTC-CDs (487 nm) and the LA-CDs (464 nm) and the wavelength of moderate emission (474 nm) for both the HTC-CDs and LA-CDs. The analysis of the scattering of a Ludox solution at the 393 nm excitation was used to determine the instrument response function.

The PL decay curves of the HTC-CDs at the 487 nm emission and the LA-CDs-10% at the 459 nm emission are depicted in figures 3(a)–(b). Using a triple-exponential function of $N(t) = A + B_1 e^{-t/\tau_1} + B_2 e^{-t/\tau_2} + B_3 e^{-t/\tau_3}$ (N(t): number of the photons emitted at time t, A: baseline/noise level, $B_i$ (i = 1, 2, 3): proportional constants for the corresponding decay functions, $\tau_i$: lifetimes) [22], we fit the PL decay curves. Both the fitting curves and residues after the curve fitting are included in figures 3(a)–(b). It is evident that the triple-exponential function well describes the lifetime behavior of both the HTC-CDs and the LA-CDs.

The lifetimes obtained from the curve-fitting are listed in table 1 and depicted in figure 4. There are three rate processes determining the lifetimes of the photon emission of the HTC-CDs and the LA-CDs under the 393 nm excitation; one is dependent on the intrinsic state of the CDs, and the other two are dependent on the extrinsic states of the CDs. The lifetime, $\tau_1$, for the rate process controlled by the intrinsic state of the CDs [22] for both the HCT-CDs and the LA-CDs is much smaller than the corresponding lifetimes, $\tau_2$ and $\tau_3$, for the rate processes.
Figure 3. TCSPC lifetime curves of xylose-derived CDs under 393 nm excitation: (a) HTC-CDs with 487 nm emission, (b) LA-CDs with 464 nm emission (The red curves represent fitting curves, and the insets represent the residues after curve fitting), and (c) overlaid emission spectra of HTC-CDs and LA-CDs under 393 nm excitation.

Table 1. Lifetimes ($\tau_1$, $\tau_2$ and $\tau_3$) of the emission lights ($\lambda_{em}$) and the relative ratios ($R_i = R_{1}\tau_1/R_{1}\tau_1 + R_{2}\tau_2 + R_{3}\tau_3$) (%) for the HTC-CDs and LA-CDs under the 393 nm excitation.

| $\lambda_{ex}$ = 393 nm | $\lambda_{em}$ (nm) | $\tau_1$ (ns) | $R_1$ (%) | $\tau_2$ (ns) | $R_2$ (%) | $\tau_3$ (ns) | $R_3$ (%) |
|------------------------|-------------------|---------------|-----------|---------------|-----------|---------------|-----------|
| HTC-CDs                | 464               | 0.60 (1)      | 33.9      | 3.03 (7)      | 48.8      | 8.62 (6)      | 17.5      |
|                        | 474               | 0.59 (1)      | 34.4      | 3.03 (6)      | 48.1      | 9.83 (6)      | 17.5      |
|                        | 487               | 0.64 (1)      | 35.1      | 3.12 (6)      | 48.4      | 9.57 (7)      | 16.5      |
| LA-CDs                 | 464               | 1.01 (5)      | 19.5      | 4.07 (4)      | 53.6      | 11.63 (6)     | 26.9      |
|                        | 474               | 1.14 (4)      | 19.8      | 4.33 (4)      | 52.8      | 11.85 (6)     | 27.4      |
|                        | 487               | 1.05 (4)      | 17.6      | 4.28 (4)      | 52.1      | 11.81 (5)     | 30.3      |

Figure 4. Lifetimes ($\tau_1$, $\tau_2$ and $\tau_3$) of three different emissions: (a) 464 nm wavelength, (b) 474 nm wavelength, and (c) 487 nm wavelength.
controlled by the extrinsic states of the CDs. The rate process associated with the lifetime of $\tau_2$ contributes about 50% to the PL decay.

Among the three emissions, the HTC-CDs exhibited the strongest emission at 487 nm with a lifetime of 0.64 ns and a relative contribution of 35.1% for the intrinsic state. For the emissions of 474 and 464 nm, there are no significant differences in the relative contribution (34.4% and 33.9% for the emission at 474 nm and 464 nm, respectively) and the lifetime (0.59 ns and 0.60 ns for the emission at 474 nm and 464 nm, respectively) for the intrinsic state. Such results suggest good uniformity in the intrinsic states for the HTC-CDs. Similar to the lifetimes for the intrinsic states, there are no remarkable differences in the relative contribution and the lifetime for the corresponding extrinsic state for the HTC-CDs.

At 487 nm emission, the deactivations due to the functional groups on the surface of CDs dominate with $\tau_2 = 3.12$ ns and $\tau_3 = 9.57$ ns and the corresponding contribution of 48.4% and 16.5%. Similar to $\tau_1$ of the intrinsic state, $\tau_2$ and $\tau_3$ do not change significantly with decreasing the emission wavelength.

The LA-CDs exhibited different characteristics in the PL decay from the HTC-CDs, as revealed in figure 4 and table 1. The LA-CDs possessed the strongest emission at 464 nm with a lifetime of 1.01 ns and a relative contribution of 19.5% from the intrinsic state. For the emissions of 474 and 487 nm, there are slight differences in the relative contribution (19.8% and 17.6% for the emission at 474 and 487 nm, respectively) and the lifetime (1.14 ns and 1.05 ns for the emission at 474 and 487 nm, respectively) for the intrinsic state. Note that the lifetime of the LA-CDs for the intrinsic state is significantly less than that of the HTC-CDs, suggesting that the laser ablation caused the change of the structures, such as the decrease in the fraction of the disorder associated with sp$^3$ carbon, through the interaction between laser and the atoms on the surface of carbon nanoparticles and introduced surface-functional groups. The decrease in the fraction of the disorder associated with sp$^3$ carbon leads to the decrease of non-radiative pathways, resulting in the decrease of the deactivation rate [22]. The deactivation process from the surface-functional groups exhibited the strongest contribution of 53.6% at 4.04 nm emission. The lifetime for the slower deactivation is 11.63 ns with a relative higher contribution of 26.9% at 464 nm emission than the HTC-CDs. There are remarkable differences of $\tau_2$, $\tau_3$ and the corresponding contributions for the emissions at 474 and 487 nm. The surface-functional groups play the dominant role in the deactivation of LA-CDs with more than 80% in contribution.

### 4. Discussion

Table 2 summarizes the PL characteristics of the HTC-CDs, Annealed-CDs and LA-CDs under the excitation of UV light of 330, 360 and 390 nm. The Annealed-CDs do not exhibit any PL characteristics under the excitation of UV light. It is evident that the HTC-CDs exhibited different PL characteristics (emission wavelength and full width at half maximum (FWHM)) from the LA-CDs.

Under the excitation of UV light of the same wavelength, the HTC-CDs emitted light with different wavelength and FWHM from the LA-CDs. Comparing the emission wavelengths of the HTC-CDs with those of the LA-CDs, we note that there always exists a blue shift in the emission wavelength under the excitation of the same UV light. The largest blue shift of 51 nm under the UV excitation of 330 nm is likely due to the relatively strong electron affinity of N atoms in the LA-CDs [32, 34] and the increase in the fraction of crystallinity introduced during the LA processing. Note that both the blue shift and the difference of FWHMs are excitation-dependent, qualitatively in accord with the results reported in literature [1, 35–37]. The PL QY of the LA-CD is $\sim2.83\%$, which is comparable with the QYs of luminescent carbon nanodots [14, 38–40] and much larger than 0.07% of the PL QY of the HTC-CDs.

As discussed in introduction, there are two competing mechanisms controlling the PL characteristics of CDs: one is the intrinsic band gap from the confined sp$^2$ domains in CDs, and the other is the extrinsic surface state [41]. Either controlling the domain size of sp$^2$ conjugation or introducing surface-functional groups on CDs can tune the PL characteristics of CDs. According to figure 1, the average particle sizes are 4.72 $\pm$ 0.72 nm and 4.23 $\pm$ 1.66 for the HTC-CDs and LA-CDs, respectively. The relative difference of the average particle sizes

| Table 2. Comparison of PL characteristics of the xylose-derived carbon nanoparticles. |
| Excitation | HTC-CDs | Annealed-CDs | LA-CDs |
|------------|---------|-------------|--------|
| Emission (nm) | FWHM (nm) | Emission (nm) | FWHM (nm) | Emission (nm) | FWHM (nm) |
| 330 nm | 459 | 123 | NA | 408 | 112 |
| 360 nm | 466 | 116 | NA | 446 | 111 |
| 390 nm | 487 | 117 | NA | 464 | 94 |
| QYs (%) | 0.07 | NA | 2.83 | |

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between the HTC-CDs and the LA-CDs is slightly larger than 0.1. For such a small relative difference, we can approximately assume that there is no significant difference in the domain sizes between the HTC-CDs and the LA-CDs. That is to say, the difference in the PL characteristics between the HTC-CDs and the LA-CDs is mainly due to the LA-induced surface-functional groups on the LA-CDs during the laser ablation in a 5 vol% NH4OH aqueous solution, which alter the mechanism controlling the PL characteristics of the LA-CDs. Note that the annealing of the HTC-CDs at high temperature likely damaged/destroyed the confined sp2 conjugation in CDs, resulting in the complete loss of the PL characteristics. The FT-IR and XPS analyses of the xylose-derived CDs were performed. Figure 5(a) shows the XPS survey spectra of the HTC-CDs, Annealed-CDs and LA-CDs. The Annealed-CDs exhibit similar XPS spectrum to the HTC-CDs without nitrogen. There are peaks at 1074.1, 534.8 and 285.6 eV for all the three type of CDs, representing Na1s, O1s and C1s, respectively. The presence of the Na1s peak is due to the residual of sodium from the deionized water and glassware. In contrast to the XPS spectra of the HTC-CDs and the Annealed-CDs, the XPS spectrum of the LA-CDs reveals the presence of nitrogen with the N1s peak at 400.1 eV, suggesting that the laser ablation of the Annealed-CDs in the NH4OH aqueous solution introduced chemical reaction between carbon nanoparticles and NH4OH to form N-contained surface-fractional groups on carbon nanoparticles. It is the N-contained surface-fractional groups on the LA-CDs that lead to the ‘re-birth’ of the PL characteristics of the LA-CDs and determine the PL behavior of the LA-CDs.

Table 3 summaries the fractions of elements presented in all the three types of CDs, which were obtained from the XPS analyses. The three types of CDs possess large fractions of carbon and oxygen. There is 6.0% of nitrogen on the LA-CDs. The fractions of oxygen content contained in the xylose-derived carbon nanoparticles are 60.4%, 54.8% and 51.3% in the HTC-CDs, Annealed-CDs and LA-CDs, respectively. The decrease in the fractions of oxygen content can lead to a tight shell of oxidized CDs with oxygen-contained groups due to the oxidation of the graphitic carbon core. The increase of the carbon content from 39.6% in the HTC-CDs to 45.2% in the Annealed-CDs reveals that annealing of the HTC-CDs at 850 °C likely damaged/destroyed the surface structures responsible for the emission of photons under UV light and increased the fraction of core structure. The same chemical elements/bonds between the HTC-CDs and the Annealed-CDs and the
disappearance of the PL characteristics of the Annealed-CDs suggest that there exist differences in the chemical states of carbon and oxygen between the HTC-CDs and the Annealed-CDs.

The deconvoluted spectra of O1s, N1s and C1s are depicted in figures 5(b)–(f). It is evident that both the HTC-CDs and annealed-CDs possess the same chemical bonds, while the fractions of the chemical bonds are different. The annealing of the HTC-CDs at high temperature did not cause the change in the chemical bonds associated with carbon, while it changed the percentage of the chemical bonds presented near the surface of carbon nanoparticles.

Figure 5(b) shows the deconvoluted XPS spectra of O1s in all the three types of CDs. The binding energies of O1s are 531.8, 533.8, and 532.8 eV for the HTC-CDs, Annealed-CDs and LA-CDs, respectively, which represent C–O and C=O bands.

Figure 5(c) depicted deconvoluted XPS spectrum of N1s in the LA-CDs. The N1s peaks at 398.6, 400.3, 401.5 and 402.4 eV reveal that nitrogen in the LA-CDs is presented mostly in the form of pyridinic, amine, pyrrolic and graphitic state, respectively [42, 43]. The blue shift in the emission wavelength of the LA-CDs in comparison to the HTC-CDs under the same UV excitation can be attributed to amine state, which can emit shorter wavelengths under UV excitation [44].

Figures 5(d)–(f) shows the deconvoluted XPS spectra of C1s in the HTC-CDs, Annealed-CDs and LA-CDs, respectively. The C1s peaks at 284.3, 284.8, 286.0, 288.2, and 289.2 eV for the HTC-CDs (figure 5(d)) can be assigned to carbon in the form of sp² C, sp³ C, C–O, C=O, and O–C=O, respectively [1, 35, 45]. The same carbon states of sp² C (284.3 eV), sp³ C (285.1 eV), C–O (286.6 eV), C=O (288.2 eV) and O–C=O (289.8 eV) are also observed for the Annealed-CDs (figure 5(e)). It needs to be pointed out that the ratio of sp³ C to sp² C for the HTC-CDs is 1.32, which is less than 1.63 for the Annealed-CDs, suggesting that the LA-CDs have smaller sp² carbon domains than the HTC-CDs. This result is qualitatively in accord with the Raman results reported by Kim et al [3] in the study of the heat effect on the structural changes of double-walled carbon nanotubes. The annealing of the HTC-CDs at 850 °C led to the formation of a large portion of defects/disordered structures through structural changes, resulting in the extinction of the PL characteristics in the Annealed-CDs.

The C1s peaks at 284.3, 285.0, 286.5, 288.0, and 289.5 eV for the LA-CDs (figure 5(f) and table 4) represent the carbon in the form of sp² C, sp³ C, C–O, C=O, and O–C=O, respectively. There is a peak at 285.8 eV, representing the C–N with a fraction of 18.5%. This result again supports the formation of N-contained surface-functional groups on the LA-CDs by the laser ablation. The peak at 294.4 eV is C–F, which is from the Teflon binder during the laser ablation and has no effect on the PL characteristics.

Table 4 summarizes the binding energies of the C1s related peaks and the fractions of various carbons in the HTC-CDs, Annealed-CDs and LA-CDs, as determined by the XPS deconvolution analyses.

Table 4. Binding energies (eV) of C1s and fractions of various carbons in HTC-CDs, Annealed-CDs and LA-CDs, as determined by XPS analysis. The binding energies are in parentheses.

| Assignment | HTC-CDs (Bing energy, eV) | Annealed-CDs (Bing energy, eV) | LA-CDs (Bing energy, eV) |
|------------|---------------------------|--------------------------------|--------------------------|
| sp² C      | 151.0 (284.3)             | 10.0 (284.3)                    | 4.2 (284.3)              |
| sp³ C      | 20.0 (284.8)              | 16.3 (285.1)                    | 14.1 (285.0)             |
| C–O        | 50.6 (286.0)              | 51.3 (286.6)                    | 49.2 (286.5)             |
| C=O        | 9.6 (288.2)               | 13.7 (288.2)                    | 0.8 (288.0)              |
| O–C=O      | 4.7 (289.2)               | 8.7 (289.8)                     | 13.2 (289.5)             |
| C–N        | —                         | —                              | 18.5 (285.8)             |

Table 4.
cm$^{-1}$ for the HTC-CDs, at 1655 cm$^{-1}$ for the Annealed-CDs and at 1668 cm$^{-1}$ for the LA-CDs [22]. In contrast to the HTC-CDs and Annealed-CDs, the LA-CDs exhibit N-H bend vibration at 1615 cm$^{-1}$ and C–N stretch vibration at 1259 cm$^{-1}$ [33, 47], which support the presence of N-contained surface-functional groups on the LA-CDs and are consistent with the XPS analysis. Both N–H bend and C–N stretch vibrations likely contribute to the photon emission under UV light.

From the above analysis and discussion, the difference in the PL characteristics for the HTC-CDs, Annealed-CDs and LA-CDs is mainly due to the surface-functional groups with and without N, since there is no significant difference in the sizes of the carbon nanoparticles. The HTC-CDs possess surface-functional groups with $\pi-\pi^*$ and $n-\pi^*$ transitions, the Annealed-CDs have only few functional groups of $n-\pi^*$ transitions, and the LA-CDs possess N-contained surface-functional groups with $\pi-\pi^*$ and $n-\pi^*$ transitions. The C-containing surface-functional groups with $\pi-\pi^*$ transition and N-contained surface-functional groups with $\pi-\pi^*$ and $n-\pi^*$ transitions contribute the PL characteristics of the HTC-CDs and the LA-CDs, respectively, and are responsible for the difference in the PL characteristics between the HTC-CDs and the LA-CDs. The presence of N in the surface-functional groups leads to the blue shifts of the emission wavelength in comparison to non-N-containing surface-functional groups in the xylose-derived CDs.

Figure 7 schematically summaries the PL behavior, which are observed in this work, for the xylose-derived CDs prepared with three different processes. It needs to be pointed out that the mechanism for the PL characteristics of the HTC-CDs remains elusive, since both the HTC-CDs and the LA-CDs exhibited similar structures with the same chemical states of elements on the surface of carbon nanoparticles. The only difference observed in the work is that the $\pi-\pi^*$ transition only appears in the HTC-CDs.
5. Conclusion

In summary, we have synthesized carbon nanoparticles from xylose via three different processes including the HTC processing at 200 °C for 6 h; the combination of the HTC processing at 200 °C for 6 h and the annealing at 850 °C in Ar for 2 h; and the combination of the HTC processing at 200 °C for 6 h, the annealing at 850 °C in Ar for 2 h and the laser ablation in a 5 vol% NH4OH solution at room temperature. The PL characteristics of the xylose-derived carbon nanoparticles have been systematically studied, and the chemical states of elements and chemical structures on the surface of the xylose-derived carbon nanoparticles have been analyzed. This work presents a feasible approach to introduce functional groups onto the surface of nanoparticles via laser ablation. The following is the summary of the results obtained in this work.

1. Under UV excitation, the HTC-CDs exhibit green emission, the LA-CDs exhibit blue emission, and there is no emission for the Annealed-CDs. The HTC-CDs exhibit the strongest emission at 487 nm under 360 nm excitation, and the LA-CDs exhibit the strongest emission at 464 nm under 390 nm excitation.

2. There is no significant difference between the particle sizes, which are 4.72 ± 0.72 nm, 4.40 ± 1.65 nm and 4.23 ± 1.66 nm for the HTC-CDs, Annealed-CDs and LA-CDs, respectively. The LA-CDs have slightly broader size distribution.

3. The annealing of the HTC-CDs at high temperature does not cause the change in the chemical bonds associated with carbon atoms, while it changes the percentage of the chemical bonds presented near the surface of carbon nanoparticles.

4. The laser ablation of the Annealed-CDs in a 5 vol% NH4OH solution at room temperature introduces N-containing surface-functional groups on the LA-CDs.

5. The C-containing surface-functional groups with the π-π* transition and N-containing surface-functional groups with the π-π* and n-π* transitions contribute the PL characteristics of the HTC-CDs and the LA-CDs, respectively, and are responsible for the difference in the PL characteristics between the HTC-CDs and LA-CDs.

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Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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