# Preparation of N-doped carbon dots based on starch and their application in white LED

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## Abstract

N-doped carbon dots (CDs) were synthesized simply and economically by a one-step hydrothermal method using starch as a carbon source and ethylenediamine (EDA) as a nitrogen dopant. The prepared CDs possess the properties of excitation-wavelength dependence and emit blue fluorescence under the excitation wavelength of 365 nm. CDs/starch composite was prepared to achieve the solid-state emission of CDs and their application in light emitting diode (LED) as fluorescent materials. White LED, with CIE coordinates of (0.33, 0.37) and correlated color temperature of 5462 K, was obtained by combining CDs/starch and ultraviolet LED light source, indicating that starch-based CDs have the promising potential in the field of optoelectronic devices.

**Key words**: starch; carbon dots; light emitting diode; white light.

# 1. Introduction

Carbon dots (CDs) are a new type of carbon materials which were first discovered in 2004 [1]. For the past decade, CDs have attracted much attention from researchers because of their promising fluorescence properties, low toxicity and low cost. So far, many different carbonaceous materials, including petroleum coke, anthracite, citric acid, pyrogallic acid, phloroglucinol, and so on, were used as carbon sources to synthesize CDs [2–8]. In recent years, the biomass-based CDs especially acquire sufficient attention because they are abundant and renewable [9]. Many biomass materials were used as raw materials to synthesize CDs, such as aminopolysaccharide chitosan, wool, wheat straw, bovine serum albumin, microalgae [10–14]. Compared with above biomass, starch can be obtained from more sources and lower cost. Starch is a polysaccharide composed of glucose units and abundant in plant seeds, tubers, tuberous roots and other organs. Starch is also rich in hydroxyl that benefit improving quantum yield (QY) of CDs [15]. Furthermore, starch has a great value of specific surface area, which facilitates the formation of CDs [16–18]. Therefore, starch is a kind of good raw materials for preparing CDs. In 2013, Chin et al. [19, 20] converted starch nanoparticles into CDs by dehydration with concentrated sulfuric acid. The CDs were used for the selective detection of $Sn^{2+}$ in water and applied in biomedical fields such as bio-imaging and biosensor. In 2016, Regina et al. [21] succeeded in converting starch nanocrystals into CDs, which can be applied in various fields, such as biomedicine, agriculture and fluorescent ink.

It has also been reported that starch-based CDs have good application prospects in many fields like biomedicine, ion detection, agriculture and fluorescent ink [19–21]. However, their application is seldom involved in optoelectronic devices. In order to expand the application field of starch-based CDs in LED, CDs based on starch were synthesized. Generally speaking, heteroatom doping, especially nitrogen doping, plays an important role in improving QY of CDs [22]. Thus, in this study, ethylenediamine (EDA) as the nitrogen dopant and starch as the carbon source were used to synthesize N-doped CDs with high QY by a one-step hydrothermal method.

The powder of N-doped CDs was mixed with starch to obtain CDs/starch composite material in order to realize fluorescence in the solid state. Finally, this composite material was combined with ultraviolet LED light source to fabricate a white LED.

## 2. Experimental

### 2.1 Materials

Starch was purchased from a local supermarket. EDA and acetone produced by Tianjin Tianli Chemical Reagent Ltd. were both of an analytical grade. Deionized water was produced in our laboratory. Polyvinyl alcohol (PVA) and quinine sulfate were produced by Sinopharm Chemical Reagent Co., Ltd. Ultraviolet LED light source was produced by Shenzhen Guanghuashi Technology Co., Ltd.

### 2.2 Characterization

Photoluminescence (PL) emission and excitation spectra were acquired by using photoluminescence spectrometer (FluoroMax-4, HORIBA Jobin Yvon, France). UV absorption spectrum was obtained by using a UV-Vis spectrophotometer (756MC, Shanghai Jinghua Instrument Technology Co., Ltd., China). The particle diameter and distribution of the CDs were detected by using a field emission transmission electron microscopy (TEM) (JEM-2100F, Japan Electronics Co., Ltd., Japan). Fourier transform infrared (FTIR) spectra were gained by operating an FTIR spectrometer (Tensor 27, Bruker Optics, Germany). Elementary composition of CDs was tested by an elemental analyzer (vario EL cube, elementar, Germany). Lifetime of CDs was detected by a transient fluorescence & phosphorescence spectrometer (FLS980, Edinburgh Instruments, UK). Thermogravimetric analysis was carried out by a thermal gravimetric analyzer (TG 209 F3, NETZSCH, Germany). Parameters of LED were obtained by using a spectroradiometer (PR-655, SpectraScan, USA).

A relative method was adopted to measure QY of CDs [23]. Quinine sulfate was used as a standard sample in this experiment and QY was calculated by Formula (1):

$$Q_c = Q_{st}(Grad_c/Grad_{st})(\eta_c/\eta_{st})^2 \qquad （1）$$

where Q, Grad and η are QY, slope and refractive index of the solvent, respectively; subscripts c and st represent CDs and quinine sulfate, respectively. The value of $\eta_c/\eta_{st}$ is approximately equal to 1.0 in this experiment because the quinine sulfate was dissolved in dilute sulfuric acid. Hence, Formula (1) can be abbreviated as Formula (2):

$$Q_c=Q_{st}(Grad_c/Grad_{st}) \qquad\qquad （2）$$

CD solutions with different optical absorbances between 0–0.1 at 365 nm were prepared. The PL spectra of CDs solutions were measured and the PL intensity between 365–700 nm was integrated, respectively. The slope can be calculated from the plot of integrated emission intensity against absorbance. Finally, the QY was calculated by Formula (2).

## 2.3 Preparation of CDs

At first, 0.65 g of starch was added into 130 mL deionized water, and then heated and stirred for two hours to form a well-distributed colloid solution (the concentration of 5 mg/mL). Next, 50 mL of starch gel was placed in an 80 mL reaction kettle with different volumes (0, 70, 140, 210 and 280 μL) of EDA. So the mixed solutions with different mass ratios of starch to EDA (1:0, 1:0.25, 1:0.5, 1:0.75 and 1:1) were obtained. The original CD solution was prepared after following reaction under 200℃ for 16 hours. After being cooled to room temperature, the purified CD solution was obtained by filtering through a disposable microporous membrane with a pore size of 0.22 μm.

The mixed solution with the optimized mass ratio of starch to EDA was prepared by the same method. The mixed solution was placed in a reaction kettle and treated by the hydrothermal method at 200℃ for different reaction times (12, 16, 20 and 24 hours) to obtain CD solution. Then the same purification treatment was adopted.

QY of CD solutions prepared under different reaction parameters were calculated and the parameters with maximum QY can be obtained by a comparison. The CD solution prepared under optimal conditions was frozen in a cryogenic preservation

cabinet at $-79\,℃$ for two hours to solidify the solution. Finally, the solid-state CDs were dried by lyophilizer for subsequent characterizations.

2.4 Preparation of white LED

The fluorescence quenching behaviour occurs in the solid-state CDs because of aggregation, which limits their application in LED. Effective dispersion of the CDs on the surfaces of starch particles can suppress the non-radiative decay processes and PL quenching induced by aggregation of CDs, so CDs/starch composite materials were prepared to achieve the fluorescence of CDs in the solid state [24]. 0.02 g of CDs, 2 g of starch and 10 mL of acetone were placed in a beaker, and then the ultrasonic method was taken for one hour to obtain a CDs/starch mixture. The CDs/starch composite materials were obtained after grinding the obtained mixture.

PVA was used as dispersing agent and binder to combine composite materials with optical lens. 1 g of PVA was added to 15 mL of deionized water and then stirred for two hours to obtain PVA solution. 30 mg CDs/starch composites were dissolved in 1 mL PVA solution and sonicated for one hours. Hence, CDs/starch composites were uniformly dispersed in the PVA solution. The inner wall of the optical lens with CDs/starch composite-PVA mixed solution was placed in an oven at $80\,℃$ for three hours to form a film. Finally, the optical lens and 365 nm ultraviolet LED light source were combined to obtain the white LED.

3. Results and discussion

3.1 Optimization of reaction parameters

Heteroatomic doping has an advantage of increasing QY by changing the surface state of CDs [22]. The dosage of EDA as the nitrogen dopant will affect the doping of N elements, which will further affect the fluorescence properties of CDs. Therefore, an effect of the mass ratio of starch to EDA on the fluorescence properties of CDs should be studied at first. The QY values of CDs prepared with different mass ratios of starch to EDA are shown in Fig.1 and Table 1, respectively. It can be seen that the

QY of CDs prepared under the mass ratio of 1:0 is only 1.74% and this kind of CDs was named as CDs-1. With an increase of EDA, QY shows a trend of first increasing and then decreasing. When the mass ratio is 1:0.5, QY of CDs reaches the maximum value of 9.65%. The increase of QY is caused by the incorporation of nitrogen-containing groups, which changes the surface state of CDs and inactivates the active sites on the surfaces of CDs. However, introducing too much nitrogen-containing groups will lead to the increase of surface defects on CDs and non-radiative transition, this will inversely reduce the QY values of CDs [25]. As a result, 1:0.5 was chosen as the optimal mass ratio of starch to EDA for obtaining CDs with high QY values.

Reaction time also has an important influence on the optical properties of CDs, so it is necessary to study the influence of reaction time on the QY values of CDs. QY values of CDs synthesized under different reaction durations are shown in Fig.2 and Table 2. It can be seen that with an increase of reaction time, QY shows a trend of first increasing and then decreasing. The QY value of CDs reaches the maximum of 9.65% when the reaction time is 16 hours. It is suggested that raw materials were not convert to CDs completely under a short reaction period. After the reaction time exceeds 16 hours, functional groups on the surfaces of CDs will be destroyed and QY of CDs will decrease [26]. Hence, 16 hours was chosen as the optimal reaction time.

Based on the above experimental results, it can be summarized that the optimal parameters of CDs prepared by hydrothermal method are that the mass ratio of starch to EDA is 1:0.5 and the reaction time is 16 hours. Finally, CDs prepared under the optimal parameters with maximum value of QY of 9.65% were selected for further research of structures, optical properties and application.

3.2 Structure and morphology of CDs

Morphology and size distribution of CDs were obtained by using TEM and the results are shown in Fig.3. The TEM image shown in Fig. 3(a) indicates that CDs are uniformly distributed. The inset is HRTEM image of CDs, from which it can be easily

found that the prepared CDs have significant lattice fringes, the interplanar spacing is about 0.22 nm, corresponding to the (100) diffraction plane of graphite carbon [27], indicating that CDs possess evident crystallinity. The histogram and Gaussian fittings of particle size distribution shown in Fig. 3(b) indicate that the size of CDs concentrated at 2.0–3.0 nm. Furthermore, the average particle diameter of these CDs is calculated as 2.22 nm.

In order to obtain the chemical bonds and functional groups present in these CDs, an analysis of FTIR was carried out and the result are shown in Fig.4. The absorption peaks at 1028 and 3366 cm$^{-1}$ correspond to C-OH and O-H contraction, which leads to good water solubility of CDs. The absorption peaks at 2941, 1651 and 1585 cm$^{-1}$ can be attributed to the presence of C-H, C=O and C=C bonds, respectively. The absorption peaks at 1585, 1340 and 3366 cm$^{-1}$ correspond to C=N, C-N and N-H contraction, and these chemical bonds proved the successful doping of N element.

An elemental analysis was taken to gain the elemental composition of CDs and the results are shown in Table 3. CDs and CDs-1 represent N-doped CDs and starch-only prepared CDs synthesized under the same optimal conditions, respectively. The presence of a small amount of N in CDs-1 may be due to an error of the instrument itself or the residual N element in the reactor. CDs have a higher content of N element compared with CDs-1, indicating that N elements from EDA have been doped into CDs. As a result, CDs have a significantly higher QY compared with CDs-1.

3.3 Optical properties of CDs

In order to study the fluorescence properties of CDs, a UV-Vis absorption spectroscopy test was taken. The UV-Vis absorption spectrum is shown in Fig.5. It can be observed that CDs solution has an absorption peak at 307 nm and this absorption peak may be attributed to the n-π* transition of the C=O bond [26].

The PL emission spectra of CD solution excited at different excitation wavelengths are shown in Fig.6. It is evident that the prepared CDs show obvious

excitation-wavelength dependence: the emission peak position and emission peak intensity altered with a change of excitation wavelength. As the excitation wavelength increases, the emission peak presents a red-shift and the emission peak intensity increases. When the excitation wavelength is 365 nm, the emission peak intensity reaches the maximum value and the emission peak is located at 441 nm. The emission wavelength continues to red-shift and the emission peak intensity gradually decreases with a constant increase of excitation wavelength. Fig.7 suggests that the excitation wavelength measured at the emission wavelength of 441 nm is 364 nm, which is consistent with the fluorescence emission spectra at different excitation wavelengths. This result indicates that CDs have the maximum fluorescence intensity at the ultraviolet excitation of 365 nm.

Many different CDs mentioned in previous reports have shown excitation-wavelength dependence [28–31]. There are two possible explanations for the excitation-wavelength dependence of CDs. The first one is that there are many different functional groups on the surfaces of CDs and these functional groups will introduce different defects on these surfaces of CDs as excitation energy traps. When different wavelengths of light irradiate on these surfaces, different energy traps will dominate the luminescence, which results in affecting the fluorescence properties of CDs. The other one is the nonuniform size of CDs. The quantum size effect caused by the size of CDs also has an impact on the fluorescence properties of CDs. The mutual effect of size effect and surface defects leads to the excitation dependence of CDs [31–35].

To testify the feasibility of CDs as phosphor for an application in white LED, their red-green-blue spectral composition was studied. The spectral composition of CDs was obtained by integrating the PL intensity of each band in the emission spectrum under the ultraviolet light with 365 nm. As shown in Fig.8, these CDs took a red-green-blue spectral proportion of 54.55%, indicating that CDs prepared from starch and EDA have a good ability of converting ultraviolet light into visible light, which provides the possibility of combining prepared CDs and ultraviolet chip to

achieve white light emission.

The time-resolved fluorescent decay curve of CDs was obtained and shown in Fig.9. The curve was tested under the excitation wavelength of 375 nm and the emission wavelength of 441 nm. These CDs exhibit double exponential decay and the fitting equation is shown in Formula (3):

$$Y(t)=\alpha_1 exp(-t/\tau_1)+\alpha_2 exp(-t/\tau_2) \tag{3}$$

where Y(t) means the sum of the individual exponential decay intensities. $\alpha_1$ and $\alpha_2$ are the proportional coefficients of decay time $\tau_1$ and $\tau_2$, respectively. The average fluorescence lifetime of CDs can be calculated by Formula (4):

$$\tau_{ave}=(\alpha_1\tau_1^2+\alpha_2\tau_2^2)/(\alpha_1\tau_1+\alpha_2\tau_2) \tag{4}$$

The various parameters required for Formula (4) and the calculation results are shown in Table 4. The result reveals that the average fluorescence lifetime of CDs is about 8.94 ns. The fluorescence lifetime of CDs consists of a short-lived component $\tau_1$ and a long-lived component $\tau_2$, which can be attributed to the intrinsic complexation of the carbon core and the surface state compound, respectively [36]. In this study, the proportionality coefficient of $\alpha_1$ is 42.28% and that of $\alpha_2$ is 57.72%, indicating that the fluorescence emission of CDs is dominated by both the carbon core and the surface state, but the fluorescence emission of surface state had a primary impact on the fluorescence emission of CDs.

3.4 Thermal stability of CDs

The thermal stability of CDs will affect the property of white LED because the general operating temperature of LED devices is about 120℃. As shown in Fig.10, the mass loss of CDs at 120℃ is only 1.5%, indicating that the CDs have a good stability at 120℃ and they can basically meet the application conditions of LED [37].

3.5 Application of CDs/starch composites in LED

To meet the need of CDs applied in LED devices, solid-state luminescence of CDs is required. Therefore, solid-state luminescent CD/starch composite materials were prepared and combined with ultraviolet LED chip to fabricate white LED. White

LED emits bright white light at the operating voltage of 3.0 V and the emission spectrum and photography are shown in Fig.11(a). The emission peak located at 400–440 nm belongs to CDs, while the emission peak located at 530–580 nm is attributed to the defects of ultraviolet LED light source [38]. The blue fluorescence emitted by the CDs is combined with the yellow light emitted by the ultraviolet LED chip to realize the white light emission of LED. The spectrum of the LED covers the entire visible region as shown in Fig.11(a). The CIE color coordinates of LED shown in Fig.11(b) is (0.33, 0.37), certifying that the prepared LED emits white light. The correlated color temperature (CCT) of LED is 5462 K, similar to the CCT in summer noon sunlight (5500 K), which indicates that the emitted white light belongs to cold white light. Based on the performance of the white LED, it is evident that the starch-based CDs can be used in white LED devices. Hence, starch-based CDs have promising potential in the field of optoelectronic devices.

## 4. Conclusions

In this study, N-doped CDs based on starch were synthesized by a simple and economical one-step hydrothermal method. EDA was used as the nitrogen dopant to increase QY of CDs. The effect of reaction time and mass ratio of starch to EDA on optical properties of CDs was investigated. The optimal reaction time and mass ratio of reactants were screened as 16 hours and 1:0.5, respectively. QY of CDs with the optimal parameters reached the highest value of 9.65%. CDs with the grain size of 2.22 nm have evident crystallinity. CDs have also shown obvious excitation-wavelength dependence, which may be attributed to the different functional groups on the surfaces of CDs and the size effect caused by quantum size. CDs have good thermal ability and meet the application conditions of LED. White LED based on CDs/starch composites and ultraviolet LED chip were fabricated and the device emits bright white light when it was operated at 3.0 V. The CIE color coordinates of LED is (0.33, 0.37) and CCT is 5462 K. Consequently, the starch-based CDs have promising potential in the field of white LED and other optoelectronic devices.

## Acknowledgments

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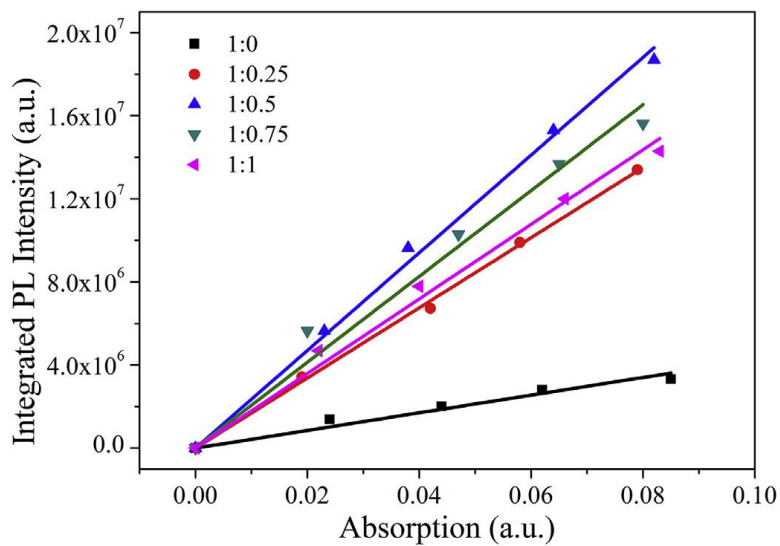
## Figures & Tables



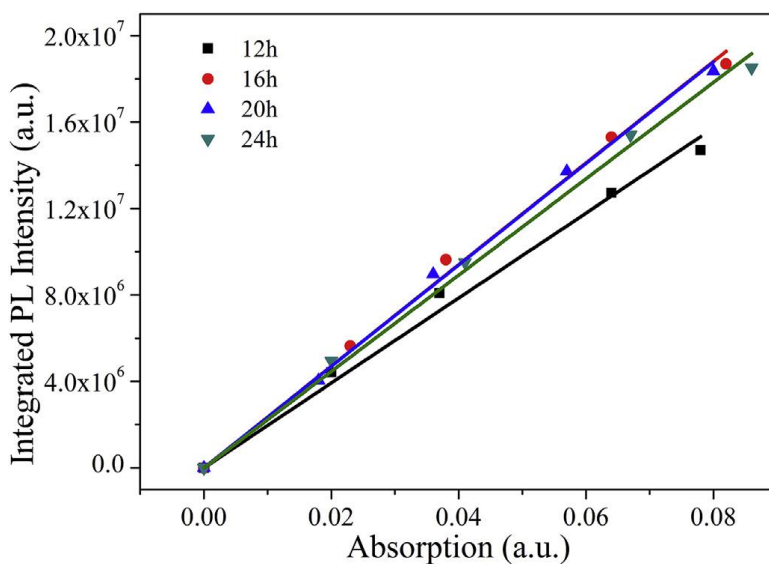**Fig. 1** QY measurements of CDs prepared at different mass ratios of starch to EDA



**Fig. 2** Measured QY values of CDs prepared at different times
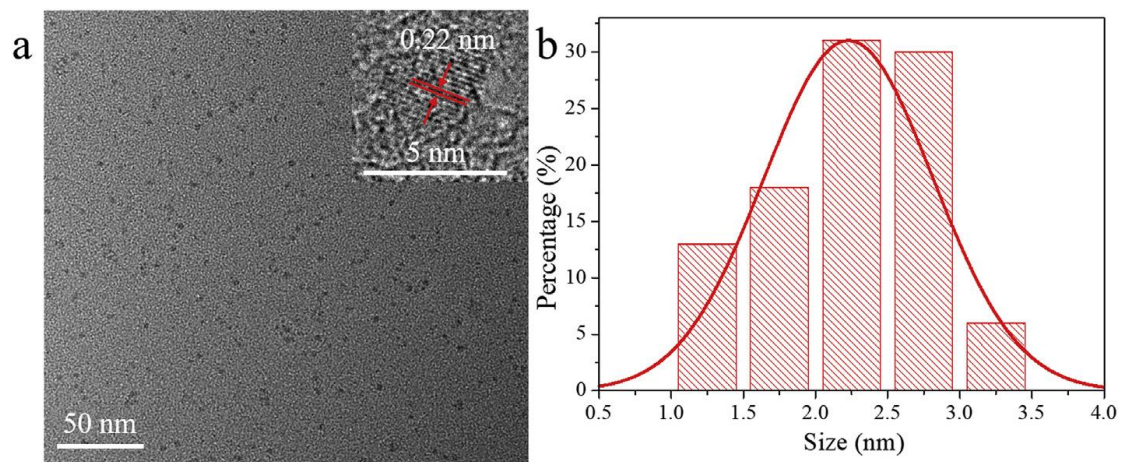
**Fig. 3** (a) A typical TEM image of CDs, inset: HRTEM image of CDs; (b) the histogram and Gaussian fittings of particle size distribution of CDs
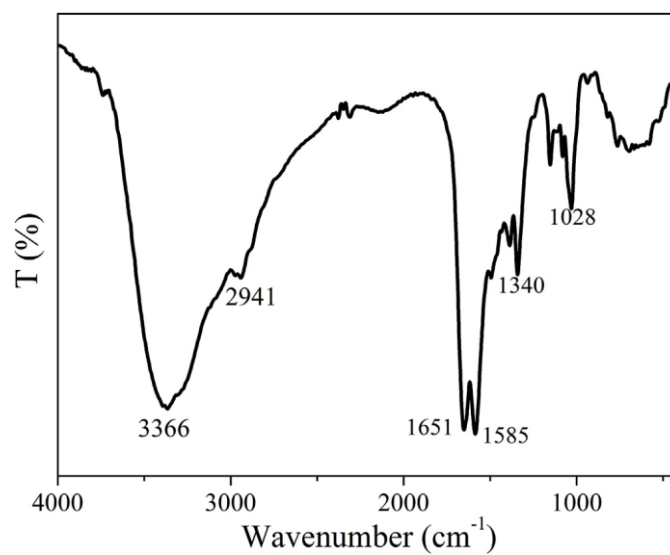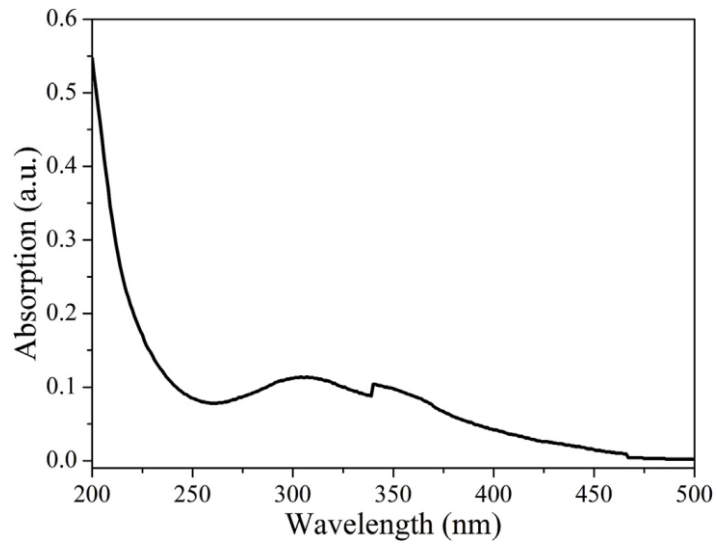


**Fig. 4** FTIR spectrum of CDs

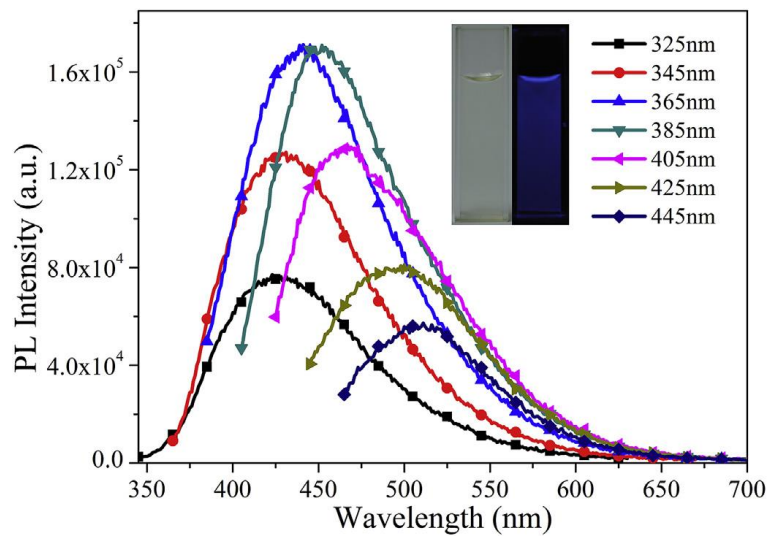**Fig. 5** UV-vis absorption spectrum of CDs



**Fig. 6** PL emission spectra of CD solution at different excitation wavelengths, inset: photographs of CD solution under sunlight (left) and UV light (right)
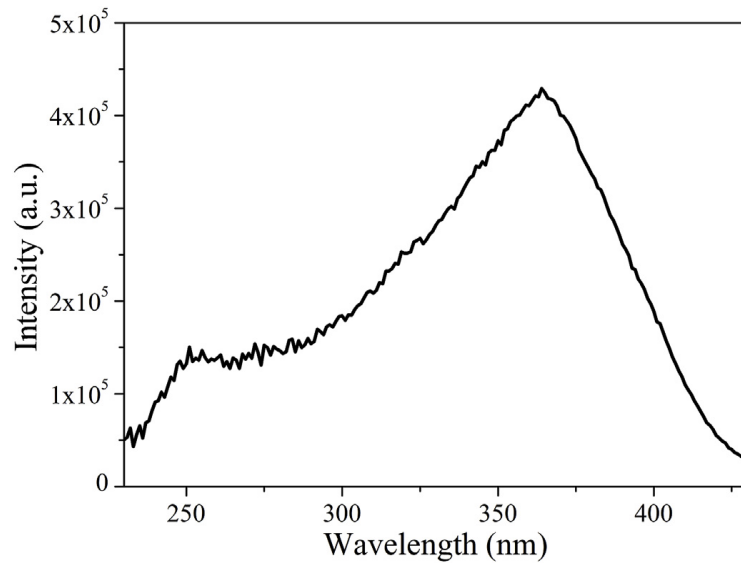
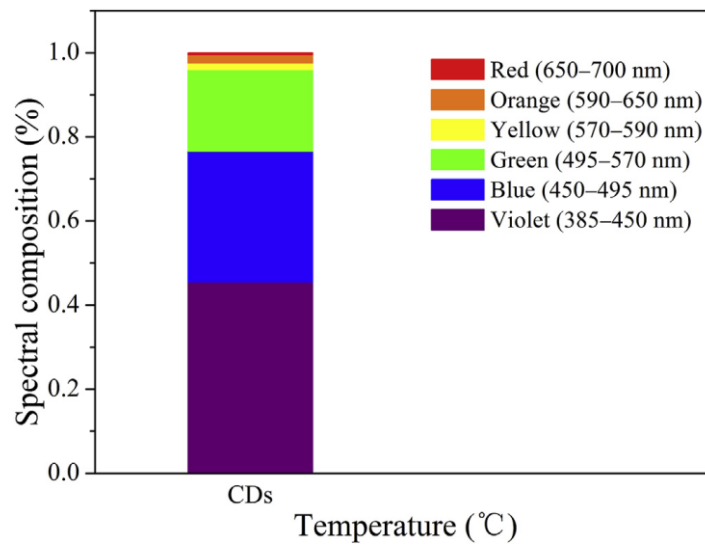**Fig. 7** Photoluminescent excitation (PLE) spectrum of CDs



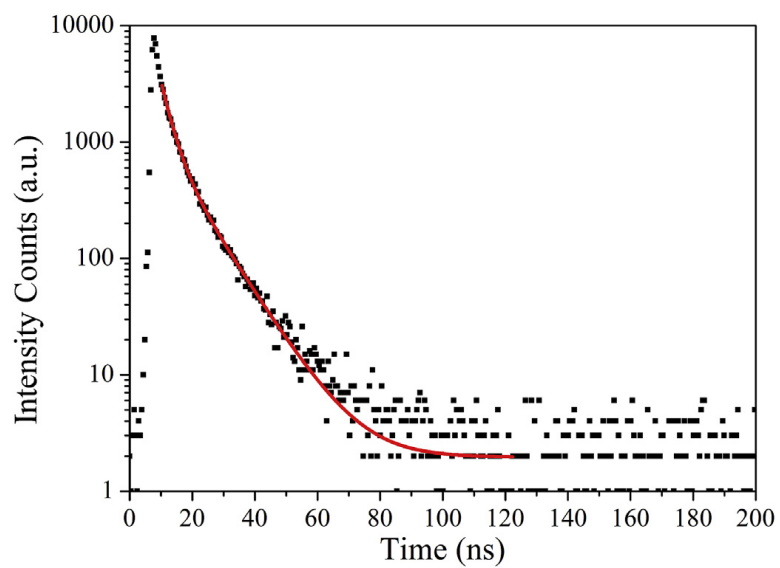**Fig. 8** Spectrum composition of CDs

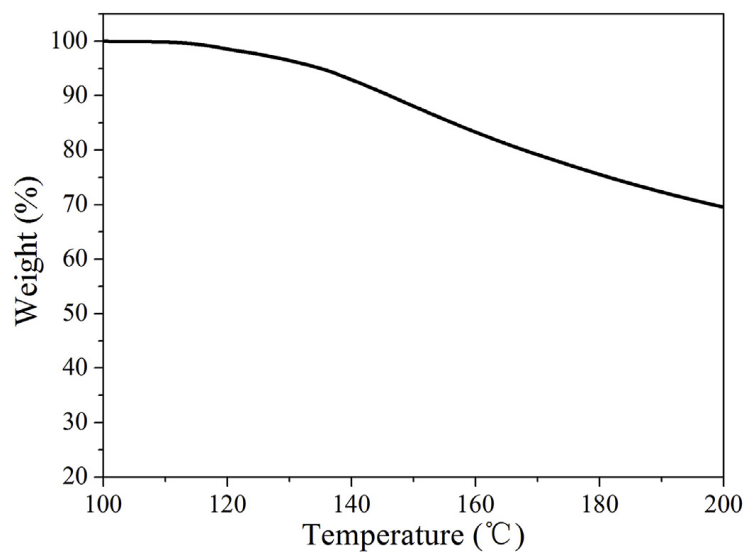**Fig. 9** Time-resolved fluorescent decay curve for CDs



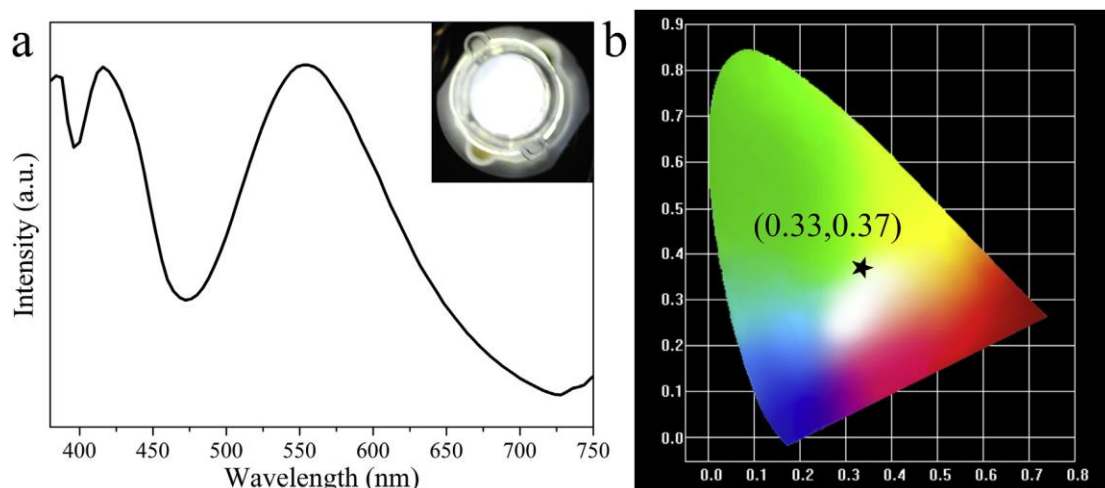**Fig. 10** A thermogravimetric analysis curve of CDs under N₂ atmosphere

**Fig.11** (a) Emission spectrum of CDs/starch composite phosphors-based white LED, inset: the photography of white LED operated at 3.0 V; (b) the CIE chromaticity coordinate for the illustrating white LED

**Table 1** Measured QY of CDs prepared at different mass ratios of starch to EDA

| Mass ratio | 1:0 | 1:0.25 | 1:0.5 | 1:0.75 | 1:1 |
|---|---|---|---|---|---|
| QY (%) | 0.74 | 6.93 | 9.65 | 8.48 | 7.37 |

**Table 2** QY of CDs prepared at different times

| Time (hours) | 12 | 16 | 20 | 24 |
|---|---|---|---|---|
| QY (%) | 8.06 | 9.65 | 9.64 | 9.15 |

**Table 3** Element contents of CDs

| Time (hours) | N | C | H |
|---|---|---|---|
| CDs | 14.26% | 37.81% | 8.01% |
| CDs-1 | 0.24% | 44.06% | 4.88% |

**Table 4** Bi-exponential fitting parameters of fluorescent decay curve of CDs

| $\alpha_1$ (%) | $\tau_1$ (ns) | $\alpha_2$ (%) | $\tau_2$ (ns) | $\chi^2$ | $\tau_{ave}$ (ns) |
|---|---|---|---|---|---|
| 42.28 | 3.12 | 57.72 | 10.24 | 1.197 | 8.94 |