Journal of Materials Chemistry B

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/materialsB

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Simultaneously enhancing up-conversion fluorescence and red-shifting down-conversion luminescence of carbon dots by a simple hydrothermal process

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

Fluorescent carbon dots (CDs) have attracted great attention in biomedical field owing to the remarkable fluorescence property, low toxicity, and excellent water solubility. Because of the "water window" effect, the CDs with upconversion fluorescence or longer wavelength downconversion fluorescence are particularly more suitable for bioimaging because they can weaken the auto-fluorescence interferences and penetrate the cell or tissue more deeply. In this study, we reported a facile method to simultaneously enhance the upconversion fluorescence and tune the downconversion luminescence of CDs from blue to green light by simply adding H_2O_2 in a hydrothermal process. The H_2O_2-treated green fluorescent CDs with excellent upconversion property showed a high yield of 34% and a quantum yield of 16.5%, and low cell cytotoxicity, which could be directly used for live Hela cell imaging.

1 Introduction

Photo upconversion (UC) is an anti-Stokes type emission. The upconversion fluorescent materials could sequentially absorb two or more photons (e.g. near infrared light (NIR)) and then emit the light at shorter wavelength (e.g. visible light).[1,2] The upconversion materials have many advantages for biological applications as they benefit from non-invasiveness, improved tissue penetration depth under NIR radiation and a high signal-to-noise ratio owing to the weak autofluorescence background generated by NIR excitation.[1,3] The trational upconversion fluorescent materials are mainly lanthanide (Ln)-doped rare-earth nano-particles.[4,5] However, the rare-earth nano-particles are hydrophobic, which must be modified for biological research.

Recently, carbon dots (CDs) have gained considerable interest in many fields, such as electrochemiluminescence (ECL) techniques, photocatalyst design, bioimaging and biosensing.[6-15] CDs were discovered accidently as a byproduct when separating and purifying single-wall carbon nanotubes (SWCNTs) fabricated by electrophoresis methods.[12,16,17] Since then, quite a few synthesis methods based on different carbon resource were developed, such as arc-discharge,[16] laser-ablation,[18] electrochemical oxidation,[19] ultrasonic,[20] microwave heating,[21] and hydrothermal method.[11] CDs exhibit excellent fluorescent properties with high photostability, high quantum yield, water solubility and favourable biocompatibility.[3] Although these CDs hold great promise in nano-biotechnology，much work is still necessary to explore the more potential of these nanomaterials in the development of advanced bioimaging or bioanalytical agents. In addition, some CDs show both size dependent downconversion photoluminescence and upconversion luminescence properties. [22,23] These properties are extremely important for the applications in bioimaging and photocatalysis.

Nevertheless, the reported CDs typically emit blue luminescence under UV irradiation.[24-26] Cells and tissues mostly emit blue light too, which would interfere with the fluorescent signals from CDs.[27,28] The development of the green or much longer wavelength fluorescent CDs is an attractive alternative to weaken the interference. In addition, in compared to blue fluorescence, longer wavelength light can penetrate into cells or tissues more deeply, which will form a more comprehensive imaging and also might be favourable for in vivo imaging. Many efforts e.g. size separation, surface modification, structure control and so on, have been taken to shift the maximum emission light from blue to longer wavelength such as green.[29-32] The ability to tune the fluorescent properties of fluorescence materials could be also useful for a number of application, such as solution phase biomolecular logic devices or sensing devices that require distinct fluorescent output signals to operate.[33-37] However, to our knowledge, the method to simultaneously enhancing the upconvertion fluorescence and red-shifting the luminescence of CDs have not been reported yet.

In the present work, a facile method was developed to simultaneously enhance the property of upconvertion fluorescence and tune the down-fluorescence colour from blue to green of the CDs by simply adding H_2O_2 in a hydrothermal process. It was observed that the amount of H_2O_2 has a large effect on the fluorescence colour. The colour of fluorescence light changed with the increase of H_2O_2. Moreover, the green fluorescent CDs show a high QY (16.5%) and low cell cytotoxicity, which can be directly used for the live human Hela cancer cells imaging without surface passivation.

2 Experimental

2.1 Chemicals

All chemicals were purchased from Sigma-Aldrich, unless otherwise mentioned. Ultrapure Millipore (Mini-Q) water (18.2 MΩ) was used throughout the experiments. Cell culture mediums were purchased from Hyclone. All glassware was washed with aqua regia (conc. HCl: conc. HNO_3, volume ratio = 3:1), and then rinsed with ultrapure water and ethanol.

2.2 Synthesis of CDs-1

CDs-1 was synthesized from ammonium citrate through a simple, convenient and one-step hydrothermal method. Briefly, ammonium citrate (0.4 g), ammonium hydroxide(50%, 3 mL), and water (20 mL) were sealed into a Teflon equipped stainless steel autoclave, which was then placed in a drying oven followed by hydrothermal treatment at 180 °C for a period of 2 h. After the reaction, the autoclave was cooled to room temperature. Then the CDs were purified through a dialysis tube (100 Da, molecular weight cutoff) for about 6 h in dark.

2.3 Synthesis of CDs-2

CDs-2 were synthesized by adding H_2O_2(30%, 2 ml) and water (15 mL) into 20ml CDs-1, then the mixture was sealed into a Teflon equipped stainless steel autoclave, placed in a drying oven, followed by hydrothermal treatment at 180 °C for a period of 2 h. After the reaction, the autoclave was cooled to room temperature. Then the CDs were purified through a dialysis tube (500 Da, molecular weight cutoff) for about 12 h in dark.

2.4 Characters of CDs

UV–vis spectra were obtained on a UV5800 Spectrophotometer. XPS analysis was carried out on an ESCALAB MK II X-ray photoelectron spectrometer using Mg as the exciting source. FT-IR spectrum was measured on an IFS 66V/S (Bruker) IR spectrometer in the range of 1540–4000 cm^{-1}. TEM measurements were performed on a HITACHI H-8100 electron microscopy (Hitachi, Tokyo, Japan) with an accelerating voltage of 100 kV. The sample for TEM characterization was prepared by placing a drop of colloidal solution on carbon-coated copper grid and dried at room temperature. Fluorescent emission spectra were recorded on a RF-5301PC spectrofluorometer (Shimadzu, Japan). QY was measured choosing Quinine sulfate in 0.1 M H_2SO_4 (literature quantum yield 0.54 at 360 nm) as a standard for CDs-1 and Rhodamine 6G in Ethanol (literature quantum yield 0.95 at 480 nm) as a standard for CDs-2. The optical densities were measured on UV–vis spectra were obtained on a UV-5800 Spectrophotometer. Absolute values are calculated using the standard reference sample that has a fixed and known fluorescence quantum yield value.

2.5 Cell culture, cytotoxicity and staining

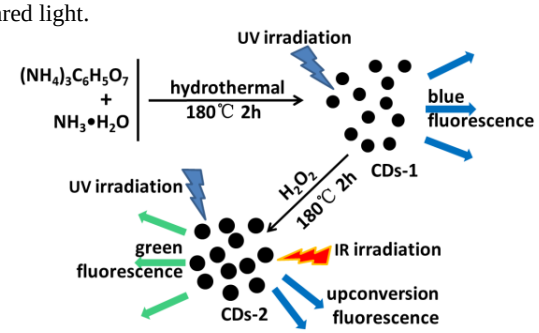
Hela (human cervical cancer cell line) cells were seeded in glass bottom culture dishes and grown in DMEM/high glucose (1×) medium supplemented with 10% (v/v) fetal bovine serum and 4 mM L-glutamine. All cells were cultured in a humid incubator at 37 °C, under an atmosphere containing 5% CO_2. Exponentially growing cells were dissociated with 0.25% Trypsin-EDTA (1×) cell dissociation medium (GIBCO).

The cytotoxicity of CDs towards Hela cells was evaluated by the CCK-8 method. The Hela cells were seeded into 96 wells culture plate and then incubated overnight in an incubator. After the culture medium was removed, CDs with different concentrations were added into each well. Cells were then allowed to incubate for another 24 h. T Then, CCK-8 (10 μl per well) solution was added in each well and incubated at 37 °C for 1 h. The absorbance was measured at 450 nm by the Enzyme standard instrument.

The cell staining of CDs was carried out as follows. A solution containing 1×10^4 cells/mL was plated in a glass bottomed culture dish (Mat Tek) and precultured for 24h. After removal of the culture medium and rinse twice with PBS (pH 7.3), cells were incubated with culture medium solution containing CDs for 24h at cell culture incubator. Before fluorescent imaging observation, the cells was washed twice with PBS and then fixed with 3.7% paraformaldehyde (Sigma) in mini-Q solution at 4 °C for 30 min to fix the state of cells, after that the fixed cells were washed once with PBS. Cells were imaged using an NIKON TE2000 inverted fluorescence microscope system.

3 Results and discussion

The blue fluorescent CDs were prepared through a simple hydrothermal process with ammonium citrate as the carbon source as shown in Scheme 1. The hydrothermal treatment could cause the pyrolyzation of the ammonium citrate, and $NH_3•H_2O$ would release NH_3 at high temperature. The produced NH_3 in the autoclave could form high pressure, promoting the decomposition of ammonium citrate into small nanoparticles to form CDs (CDs-1) .[38,39] The as prepared CDs emit blue light and do not show the upconversion fluorescence. Subsequently, H_2O_2 was added to the reaction system accompanied by a hydrothermal process. The oxidization with H_2O_2 through hydrothermal process influenced the optical properties of the CDs, and the color of the fluorescence shifts from blue (CDs-1) to green (CDs-2), and the upconversion fluorescence was also come out when excited with infrared light.



Scheme 1. Schematic illustrations of the preparation process of CDs. The CDs-1 was directly prepared through a hydrothermal process using ammonium citrate and $NH_3•H_2O$ as the precursors. When the CDs-1 was treated by H_2O_2 through a hydrothermal process the obtained CDs-2 emits green flourescence under UV irradition and upconversion fluorescence under IR irradiation.

The effect of oxidization from H_2O_2 on the UV/Vis absorption and downconversion emission spectrum of CDs is shown in Figure 1. Figure 1b showed the absorption bands of CDs-1(blue line) at ca. 235nm and 334 nm, which is ascribed to the π-π*

transition of C=C and n-π* transition of C=O, respectively.[40] After treated with H_2O_2, the peak moved to 265nm and 318nm (CDs-2, green line). Figure 1c and 1d shows the fluorescent spectrum of CDs-1 and CDs-2 at different excitation wavelengths between 330 nm and 400nm. CDs-1 show two emission peaks located at 431 nm and 483 nm, respectively. The two peaks almost did not shift when the excitation wavelengths change, which is similar to what's observed in the previously reported CDs.[11,39] Some studies reported that the CDs synthesised from citric acid or ammonium citrate has excitation-independent fluorescence property.[11,39] The fluorescent peak at 483 nm of CDs-1 mainly results from the surface-doped nitrogen atoms. For CDs-2, in addition to the fluorescent peak at 431nn, another peak, instead of 483 nm, was found as a series of peaks shift between 495 nm and 580 nm with almost the same intensity when the excitation wavelengths change. This excitation-dependent fluorescence property is similar to the characteristics of some other reported CDs.[14,41] which may be attributed to different energy levels associated with different "surface states" formed by different functional groups.[42] The two peaks of the CDs could be attributed to the inner core and the outer shell of the CDs. When CDs-1 was oxidised by H_2O_2, the inner core of the CDs was not affected, so the peak at 431nm was reserved; however, the outer shell of the CDs could be oxidised by H_2O_2, the structure of surface nitrogen doped was oxidised, so the peaks changed. Accompanying with the red shift of the fluorescence was the quantum yield decreased from 25.7% (CDs-1) to 16.5% (CDs-2) (Table 1). In spite of a QY decrease, the QY yield of the CDs-2 was still much higher than most of the reported green fluorescence CDs.[38,43]

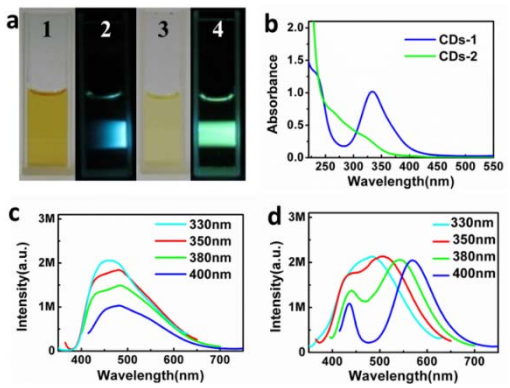


Figure 1. a), Photograph taken without and with UV irradiation (365 nm) for CDs-1 (1, 2) and CDs-2 (3, 4); b), UV-Vis absorption spectrum of CDs-1(blue line), and CDs-2(green line); c), and d) fluorescence spectra at different excitation wavelengths of CDs-1, and CDs-2, respectively.

Table 1. The typical characteristics of the two CDs.

No.	Yield(g)*	QY(%)	Flourescent Peak(nm)	Elemental composition (C:N:O)
CDs-1	0.32	25.66	447	62:9:29
CDs-2	0.34	16.5	530	56:9:35

* per gram ammonium citrate

Remarkably, CDs-2 also show good upconversion properties in addition to the above discussed downconversion fluorescence property when excited by various long wavelength lights (from 700 to 1000 nm). In contrast, CDs-1 do not have distinct upconversion property as show in Figure 2. A few studies have reported CDs with upconversion fluorescent,[22,23] but no methods have been developed to enhance the upconversion fluorescence. The upconversion fluorescent spectra show that the wavelength of the upconversion emission peaks were located around 483 nm. The maximum intensity upconversion peak apears under 850 nm excitation. In contrast, for CDs-1, the upconversion peaks were almost invisible. This upconverted flourescent property of CDs-2 could be assigned to a multiphoton active process similar to the reported CDs.[1] The results suggest that the green fluorescence CDs-2 may be used as a powerful reagent for cell imaging with upconversion fluorescent microscopy as well as for an efficent photoelectric energy conversion device.

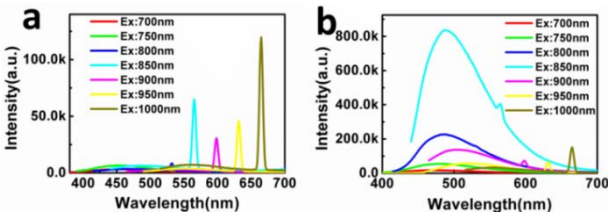


Figure 2. Upconverted fluorescent properties of CDs. Fluorescent emission spectra for the CDs-1 a) and CDs-2 b) at various excitation wavelengths from 700 nm to 1000 nm.

TEM was used to illustrate the effects of H_2O_2 on the particle size. Figure 3 show TEM images of the CDs-1 and CDs-2,respectively. As shown in Figure 3, combining with the corresponding particle size distribution histograms (inset) indicate that CDs-1 are in the range of 1.5 to 3 nm with a mean diameter of 2.63 ± 0.47nm (Figure 3a). In contrast, when the CDs-1 was treated with H_2O_2 through hydrothermal process to form CDs-2, the mean particle size increases to 3.94 ± 0.68 nm (Figure 3b). The results also conform with the verdict of previous studies, which suggested that the carbon dots with larger size emit fluorescent at longer wavelength.[44] The TEM images also reveal that the two CDs are almost spherical, mono-dispersed and show a narrow distribution size.

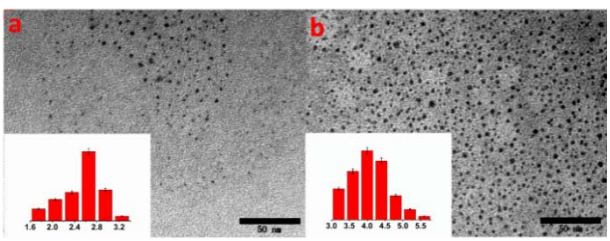


Figure 3. The TEM images of the CDs-1 a), CDs-2 b).The inset histograms are the size distribution of the CDs, and the mean diameters were 2.63±0.47nm, and 3.94±0.68nm for CDs-1, and CDs-2, respectively.

The overall composition and the surface elemental analysis of the CDs was further obtained from the X-ray photoelectron spectroscopy (XPS) (see Figure S1 in the Supporting

Information).The XPS spectrum results of the CDs (Figure S1a, e) indicate that CDs-1 and CDs-2 are mainly composed of carbon, nitrogen, and oxygen (Table S1). The highresolution C_{1s} spectrum of CDs-1 and CDs-2 shows four main peaks around 284.0 eV, suggesting the presence of C-C, C-O, C-N and C=N/C=O groups.[45-47] The high-resolution N_{1s} spectra around 400.0 eV of CDs-1 and CDs-2 (Figure S1c, g) reveal three relative nitrogen species of the C-N-C, N-$(C)_3$,[9] and N-H bands. And for CDs-2, another peak at 407.0 eV is also observed, which is attributed to the presence of -NO_3.[48] The high-resolution O_{1s} spectra around 531.8 eV of CDs-1 and CDs-2 (Figure S1d, h) reveal the presence of C=O and C-O-C/C-O-H units.[45-48] Fourier transform infrared (FTIR) spectra (Supporting Information, Figure S2) further confirm the presence of a series of CN, CO and NO units. Comparing the peaks around C_{1s}, N_{1s}, and O_{1s}, and the elemental analysis results (Table S1) from XPS, we can find that CDs-2 have much greater relative amount of C=O groups, and -NO_3, indicating that the surface of CDs-2 have higher oxidation state than CDs-1, which may change the surface energy level distribution and enhance/shift the flouresence.

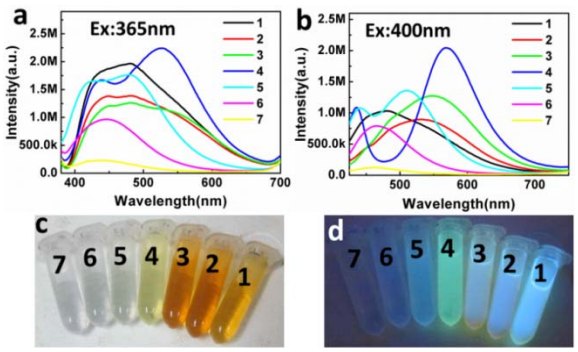


Figure 4. Fluorescent properties and photographs of CDs prepared with different amounts of H_2O_2. Fluorescent emission spectra of blue flourescent CDs after oxidization treatment with different stoichiometric ratio of H_2O_2 when excited at 365 nm a), and excited at 400 nm b). The photographs of the CDs taken under white light c) and UV light d). Number meaning: 1: without H_2O_2, CDs-1; 2: 0.5 ml H_2O_2; 3: 1 ml H_2O_2; 4: 2 ml H_2O_2, CDs-2; 5: 4 ml H_2O_2; 6: 8 ml H_2O_2; 7: 16 ml H_2O_2.

Surface state is a key factor to the luminescence of the CDs. A few studies reported that the flourescence of CDs could be tuned with reduction.[49,50] The flourescence of the CDs would be greatly enhanced and blue shifted when the CDs were reduced by sodium borohydride or photothermal treatment. [49,50] And the flourescence of the CDs would be quenched or red shifted, when the CDs were oxidized.[51] However, H_2O_2 are always used as the flourescent quenching agent.[49,52] To our surprise, H_2O_2 could change the surface structure of CDs and tune the flourescence color of CDs through a simple hydrothermal process. To further illustrate the effects of H_2O_2 amount on the fluorescent properties, the evolution of the corresponding flourescent spectra (excited at 365 nm) of blue flourescent CDs after oxidization treatment with different stoichiometric ratio of H_2O_2 is shown in Figure 4a. Both the fluorescent intensity and peak position for CDs largely changed after treated with 0.5, 1.0, 2.0, 4.0, 8.0 and 16.0 ml 30% H_2O_2 solution. Some water was added to get a 36 ml of the final solution volume, and the corresponding final concentration values of H_2O_2 are 0.417%, 0.833%, 1.67%, 3.33%, 6.67%, and 13.3%, respectively. When excited with the ultraviolet light around 365nm, the as-prepared CDs-1 samples showed broad flourescent peak, ranging from 435 to 485 nm. The flourescent peaks around 530nm gradually appeared as a small quantity of H_2O_2 was added. When the quantity of the added H_2O_2 is higher than 4ml, the peak around 530nm disappeared, and the intensity of the peak ranging from 420 to 480 nm discrease. The more clear trend of the change could be observed when CDs were excited with the ultraviolet light around 400nm (Figure 4b). The corresponding photographs of the flourescence from CDs solutions at different stoichiometric ratio of H_2O_2 are shown in Figure 3c and Figure 3d. The flourescent colors of these CDs can be gradually tuned from the original strong blue in the assynthesized CDs-1 solution (Figure 4d $1^{\#}$) to the green in the CDs-2 solution (Figure 4d $4^{\#}$) after treated with H_2O_2 less than 1.67%, then turn into weak blue utill almost no fluorescence after treated with H_2O_2 more than 4ml(Figure 4c $5^{\#}$). The results indicate the significant effects of H_2O_2 amount on the fluorescent properties and the optimum stoichiometric amount of H_2O_2 to obtain green flourescent CDs-2 is 1.67%.

For future biological applications, the potential cytotoxicity of the CDs was evaluated after the HeLa cells were treated with different doses of C-dots by a CCK-8 assay. As shown in Figure S3, no visible reduction of cell viability was found after 24h treatment with high concentrations of the CDs (e.g. 2mg/ml, Figure S3a), and even after 72h treatment, the mortality rate was also very low (Figure S3b).The cell toxicity of the CDs was much lower than what's reported in similar nanoparticles such as semiconductor quantum dots.[53] However, more studies of safety issues are still needed for future practical biomedical applications.

To demonstrate the bio-applications of the CDs-2 as flourescent probes, we further investigated the performance of fluorescent cell labels. As shown in Figure 5, the fluorescence images clearly indicated that the CDs entered the cytoplasm of Hela cells. The results indicate that the green fluorescence CDs-2 can be directly used for cell imaging and no further modification is needed.

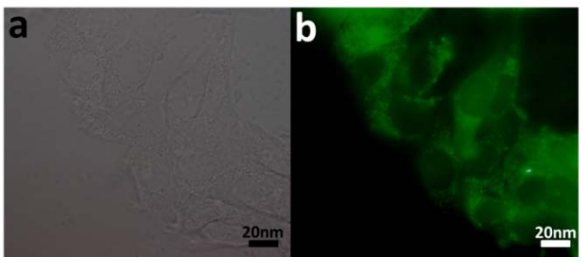


Figure 5. Bright field a) and fluorescence b) microphotographs of live Hela cells treated with the CDs-2

4 Conclusions

In conclusion, we have developed a simple method to largely enhance the upconversion flourescence of CDs while modulating the downconversion flourescence color from blue to green. When oxygenized by H_2O_2, the fluorescent color could be red-shifted. The fluorescent color is largely dependent on the amount of H_2O_2. The green flourescence CDs tuned in this way show both high yield and quantum yield, and can be directly used for live cell imaging. The small sized carbon-based quantum dots with both upconversion and downconversion emission provide a new choice for live cell staining, and have a large potential application in biomedical diagnosis and treatment. Further more, the ability to readily tune the fluorescent properties of carbon dots might be useful in some other applications including solution phase biomolecular logic devices or sensing devices that require distinct fluorescent output signals to operate.

Acknowledgements

This work was supported by the State Key Project of Fundamental Research (Grants 2014CB931900 and 2012CB932504) and the Chinese Academy of Sciences ("Hundred Talents Project").

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† Electronic Supplementary Information (ESI) available: XPS survey scan of CDs, the table of XPS detailed information of CDs, FT-IR of CDs, Viability of the HeLa after 24 h and 72h incubation with the CDs-2. See DOI: 10.1039/c000000x/

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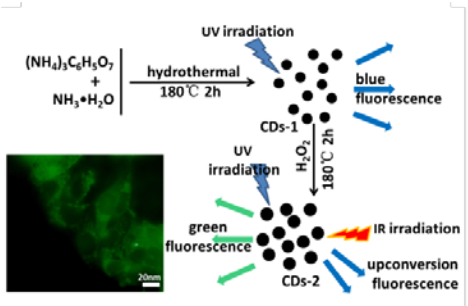
TOC



Simultaneously enhancing up-conversion fluorescence and red-shifting down-conversion luminescence of carbon dots has been achieved by a simple hydrothermal process.