Talanta 117 (2013) 196–202

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

A new hydrothermal refluxing route to strong fluorescent carbon dots and its application as fluorescent imaging agent

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ARTICLE INFO

Article history:
Received 24 May 2013
Received in revised form
2 September 2013
Accepted 2 September 2013
Available online 11 September 2013

Keywords:
Hydrothermal refluxing
Tris
Lactose
Fluorescence
Carbon dots
Imaging

ABSTRACT

Due to their unique optical and biochemical properties, the water-soluble fluorescent carbon dots (CDs) have attracted a lot of attention recently. Here, strong fluorescent carbon dots with excellent quality have been synthesized by the hydrothermal refluxing method using lactose as carbon source and tris (hydroxymethyl) aminomethane (i.e. Tris) as surface passivation reagent. This facile approach was simple, efficient, economical, green without pollution, and allows large-scale production of CDs without any post-treatment. TEM measurements showed that the resulting particles exhibited an average diameter of 1.5 nm. The obtained CDs possess small particle sizes, good stability in a wide range of pH values (pH 3.5–9.5), high tolerance of salt concentration, strong resistibility to photobleaching, and a fluorescent quantum yield up to 12.5%. The CDs were applied to optical bioimaging of HeLa cells, showing low cytotoxicity and excellent biocompatibility.

1. Introduction

Carbon is one of the most abundant elements in nature. Carbon-based nanomaterials (including carbon nanotubes, fullerenes, nanodiamond, carbon nanoonions and nanofibers) have promising applications in nanotechnology, biosensing and drug delivery. Among these various forms of carbon nanomaterials, carbon nanoparticles represent a new but unique class of functional materials that warrant further and more thorough investigation. Since 2006, Sun et al. [1] found a new fluorescent nanoparticals named as carbon dots (CDs), CDs have been attracting more and more interests in the past few years due to their unique optical and biochemical properties.

Compared with traditional organic fluorchromes, CDs have a relatively high fluorescence stability, resistance to photodegradation and photobleaching, as well as excitation wavelength dependent photoluminescence (PL) behavior [1]. Meanwhile, widely used quantum dots (QDs) as fluorescent probe arouse some serious concerns about health and environment since recent years due to the use of heavy metals as the essential elements, which limits their wide applications [2–5]. On the contrary, CDs exhibit some advantages over quantum dots such as excellent biocompatibility, low cytotoxicity and small size, which opens a promising flat to biosensing [6–9] and bioimaging [10–13]. Carbon dots also have been applied in many other areas based on its excellent fluorescent characters, such as fluorescent ink [14] and converting material in white light emitting diodes [15].

Significant efforts have been devoted to the synthesis of CDs. A variety of preparation methods have been developed either by physical or chemical means including arc-discharge [16], laser ablation of a carbon target [1,17], electrochemical oxidation [18,19], combustion/thermal polymerization [20,21], chemical oxidation [11,22–25], supported synthesis [26], microwave heating [27,28], and ultrasonic [29].

However, these approaches usually involve complex or post-treatment processes, or require expensive raw materials and strict synthetic conditions. Likely, they need further surface modification with poisonous amine-terminated compounds, or strong acids (sulfuric acid, nitric acid or perchloric acid). In addition, the quantum yield of most of these single-step methods is too low ($<10\%$) with few exceptions [28,30–33]. Thus, simple, efficient, and large-scale synthesis of strong fluorescent carbon nanoparticles with high quantum yield and their isolation, purification, and functionalization are very challenging.

Among all of those preparation methods, we chose the hydrothermal method. Hydrothermal route is a promising and quite attractive one because it directly leads to oxygen-containing (e.g. hydroxyl group, carboxylic group) or amino group functionalized carbon dots with good stability and biocompatibility, and careful

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http://dx.doi.org/10.1016/j.talanta.2013.09.003

selection of carbon source and surface modifier make it possible to better control of size, shape, physical and optical properties. In addition, the operation of fluxing an aqueous solution at 100 °C is quite simple. Since there is no need of high temperature, high press, corrosive solution or toxic reagents, it is much safer for experimenter and the environment. And there is no report on the synthesis of fluorescent carbon dots by the directly refluxing method before.

In the present work, we established a single-step hydrothermal route to prepare strong fluorescent CDs by refluxing a mixed solution containing lactose and Tris at 100 °C for 24 h. We chose innocuous Tris as surface passivation reagent instead of poisonous amine-terminated compounds for the first time. The synthesis condition is mild without strong acid, alkali, additive or high temperature. The process is simple, efficient, economical, easy to control, propitious to large-scale preparation and it reduces the pollution of the environment greatly. The prepared fluorescent CDs exhibit excellent water-solubility, mono-disperse, small particle size (~1.5 nm), strong fluorescence and high fluorescence quantum yield up to 12.5%. We used the CDs as fluorescent probe for optical imaging in HeLa cells, and the in vitro cytotoxicity study showed the CDs pose low toxicity effects.

2. Experiment section

2.1. Materials and reagents

α-D-lactose, D-glucose, sucrose, tris(hydroxymethyl) aminomethane (Tris), diethylene glycol, diethanolamine, 2-(2-aminoethoxy) ethanol were analytical grade reagents purchased from Alfa Aesar and used as supplied. Hydrochloride acid (HCl, A.R., 36 wt%), sodium hydroxide (NaOH), phosphoric acid (H_3PO_4), monosodium orthophosphate (NaH_2PO_4) and disodium hydrogen phosphate (Na_2HPO_4) were commercially available from Tianjin Beifang Tianyi Chemical Reagent Company. Dulbecco's modified Eagle medium (DMEM) was purchased from Invitrogen Corporation. Fetal bovine plasma was purchased from Dingguo Corporation (Beijing, China). 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide (MTT) was obtained from Sigma-Aldrich. The water used throughout all experiments was ultrapure water which was obtained from an AWL-0502-U super pure water system (Aquapro, China).

2.2. Instruments

Fluorescence spectra were obtained by an F-4500 fluorescence spectrophotometer (Hitachi, Japan). Absorption spectra were gotten with a UV-2450 UV–visible spetrophotometer (Shimadzu, Japan). TEM images were acquired by using a TECNAI-G2F20 transmission electron microscope (FEI, Holand) operating at an acceleration voltage of 200 kv. For TEM imaging, the CDs dispersions were dropped directly onto a copper grid with an amorphous carbon coating. X-ray photoelectron spectroscopy (XPS) was conducted using a Kratos Axis Ultra DLD spectrometer (Kratos, U.K.) employing a monochromated Al-Ka X-ray source ($h\nu = 1486.6$ eV). The peak position was internally referenced to the C 1s peak at 284.6 eV. The cell imaging was operated by a Leica Tcs sp^5 confocal fluorescence microscope (Leica, Germany) with excited under 405 nm. The optical densities (OD) at 490 nm were measured in a BIO-RAD iMark coelosphere reader (BIO-RAD, USA).

2.3. Synthesis of luminescent CDs

The luminescent CDs were synthesized by a single step hydrothermal route. A schematic illustration was shown in Fig. 1. In a typical procedure, 0.125 g of lactose and 2.0 g of Tris were dissolved in 40 mL pure water. The pH of the mixed solution was about 10.5 and it was hydrothermally refluxed at 100 °C with stirring for 24 h. The solution turned from colorless into yellow. After cooled down to room temperature, we neutralized the pH with hydrochloride acid, and dialyzed (MW 1000) the solution against water for two days. The CDs decorated with abundant hydroxyl groups were obtained.

2.4. Fluorescence imaging

The potential for bioimaging of CDs was tested using HeLa cells, a human cervical cancer cell line. Approximately 10^5 cells were deposited on each coverslip (diameter = 14 mm) to form a sparsely distributed layer of cells. This ensures good exposure to CDs. Cells were cultured using Dulbecco's modified Eagle's medium (DMEM) growth medium with 10% fetal bovine plasma at 37 °C under 5% CO_2. All the cells were incubated until approximately 70% confluence was achieved. Then the mixture of 0.2 mg ml^{-1} CDs in DMEM medium was added to each well. After 4 h incubation in 5% CO_2 at 37 °C, the cells were washed three times with phosphate-buffered saline (PBS) to remove extracellular CDs and then fixed with 4% paraformaldehyde. The coverslips were sealed with 90% glycerin before imaging with the confocal fluorescence microscope (Leica Tcs sp^5).

2.5. The in vitro cytotoxicity study of CDs

The cell viability was evaluated on HeLa cells using MTT assay. The cells were exposed to 0.5–4 mg mL^{-1} of CDs for 48 and 72 h, respectively. The cell survival rate can be calculated by the absorbance at 490 nm. 100 μL of 1×10^6 cells mL^{-1} cells were seeded into 96-well culture plates and allowed to grow over 12 h (the cells reached 70–80% confluence). The medium was then replaced with 100 μL fresh DMEM contained different concentrations of CDs (0, 50, 100, 200, and 400 mg mL^{-1}, respectively). The cells were allowed to grow for 48 or 72 h. Then 20 μL MTT

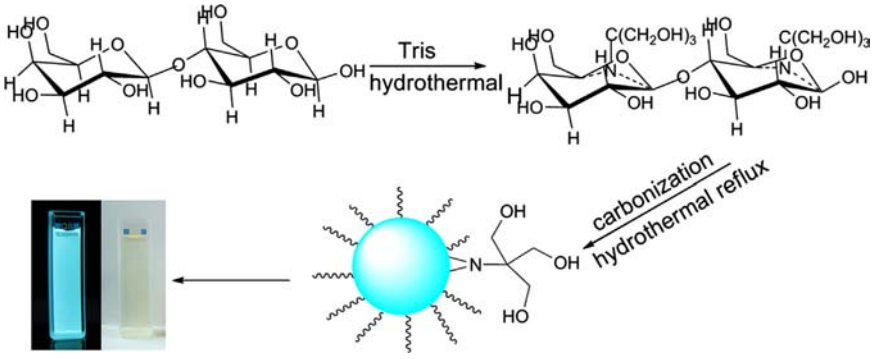


Fig. 1. A schematic illustration of the preparation procedure of photo-luminescent CDs by the hydrothermal refluxing method [34].

reagents (5 mg mL^{-1}) were added into each well and incubated for another 4 h. The medium was removed and 150 μL dimethyl sulphoxide was added to completely liberate the formazan crystals. The absorbance at 490 nm was measured.

3. Results and discussion

3.1. Characteristics of luminescent CDs

We synthesized the CDs by the hydrothermal refluxing method. The formation of CDs was first confirmed by TEM measurements. Fig. 2 shows a representative TEM micrograph of the CDs. It can be seen that the particles are mostly of spherical shape and typical amorphous carbonaceous structure with no discernible lattice were observed. This result is similar to that of many other reported papers [11]. The diameters of the CDs distribute narrowly, with an average value of 1.5 nm, as depicted in the size histogram.

The surface composition of the resultant nanoparticles was characterized by XPS techniques. The XPS spectrum of the nanoparticles was shown in Fig. S1. It exhibited three peaks at 285.8, 398.8 and 531.8 eV, which were attributed to C1s, N1s, and O1s, respectively. Element analysis confirmed the CDs contained mainly elemental carbon and oxygen (C 42.38%, H 6.93%, N 5.04%, O (calculated) 45.65%). And the presence of hydroxyl group was manifested by means of Fourier-transform infrared (FTIR) spectroscopy (see Fig. S2). The CDs exhibited characteristic absorption bands of O–H stretching vibrations at 3385 cm^{-1}, C–H stretching vibrations at 2937 cm^{-1}. Asymmetric and symmetric stretching vibrations of C–O–C in the carboxylate groups were detected at about 1400 and 1057 cm^{-1}. We also observed two broad peaks at 1623 and 1576 cm^{-1}, indicating the presence of an amide bond [21,34].

3.2. The fluorescent properties of the as-synthesized CDs

The fluorescent properties of these CDs synthesized via the aqueous solution hydrothermal pathway were investigated. Fig. 3a shows the typical absorption and PL spectra of the as-synthesized CDs. There is an absorption peak at about 320 nm. The CDs can be excited in a wide range (from 300 nm to 470 nm). But they emitted at a similar wavelength when excited from 380 nm to 470 nm and emitted a little differently when excited from 300 nm to 360 nm (Fig. 3b). The maximum emission intensity can be obtained when excited at 410 nm with a maximal emission at 523 nm. The full-width at half-maximum (FWHM) was relatively narrow (~90 nm), suggesting a relatively small size distribution of the particle (as shown in Fig. 3c), which was consistent with the TEM results. The obtained CDs showed strong up-conversion fluorescence simultaneously (Fig. 3d). When excited from 750 nm to 900 nm, the up-conversion fluorescence were also emitted at similar wavelength (λ_{em}=523 nm) with a maximal excitation wavelength near 850 nm.

The obtained CDs showed considerable photostability with the emission intensity decreasing by only 2.8% after 400 min of continuous excitation at 410 nm (see Fig. S3). An aqueous solution of the CDs was stable for at least six months, and the fluorescence intensity decreased only 4.8% without any precipitate at 4 °C. The quantum yield of CDs was calculated with quinine sulfate (excited at 410 nm) as the reference compound [17,35]. The fluorescence quantum yield of CDs has a high value up to 12.5%, which was either comparable or superior to previously reported carbon dots [1,8,17–21].

3.3. Selection of carbon sources and surface passivation reagents

We investigated several kinds of carbon sources, such as lactose, glucose [27,29], sucrose [36], citric acid [20,21,33], L-ascorbic acid [37] and EDTA [30]. The results showed that the CDs could be synthesized successfully with only lactose or glucose. What unexpected was that lactose and sucrose exhibited rather different results even though they are isomers ($C_{12}H_{22}O_{11}$, see Fig. 4). We can gain strong fluorescent CDs with lactose, but no fluorescence was found with sucrose. This may have two reasons: first, lactose can be passivated with Tris in a form of pyrrolic ring [34] as shown in Fig. 1. Oppositely, the structure of sucrose (see Fig. 4a) contains a planar tetrahydrofuran ring which makes the formation of pyrrolic ring impossible, and the α-1,4 glycosidic bond adds difficulty to passivate carbon core since it leads the two hydrogen atoms connected to 1-, 5- carbon atoms arrange on two sides of the ring (as shown in Fig. 4a). Second, it may attribute to the active hydroxyl group in lactose's semiacetal structure while there is no such structure in sucrose. Under such a mild condition we reported here, this active hydroxyl group may have a big influence on the formation of the carbon core because it induces the condensation reaction between saccharides before they are carbonized. We also found that lactose was better than glucose at the same amount. As shown in Table 1, the quantum yield of CDs increased about 45.3% (from 8.6% to 12.5%) when we replaced glucose with lactose as a carbon source. How did this happen? We suppose this may be caused by reasons

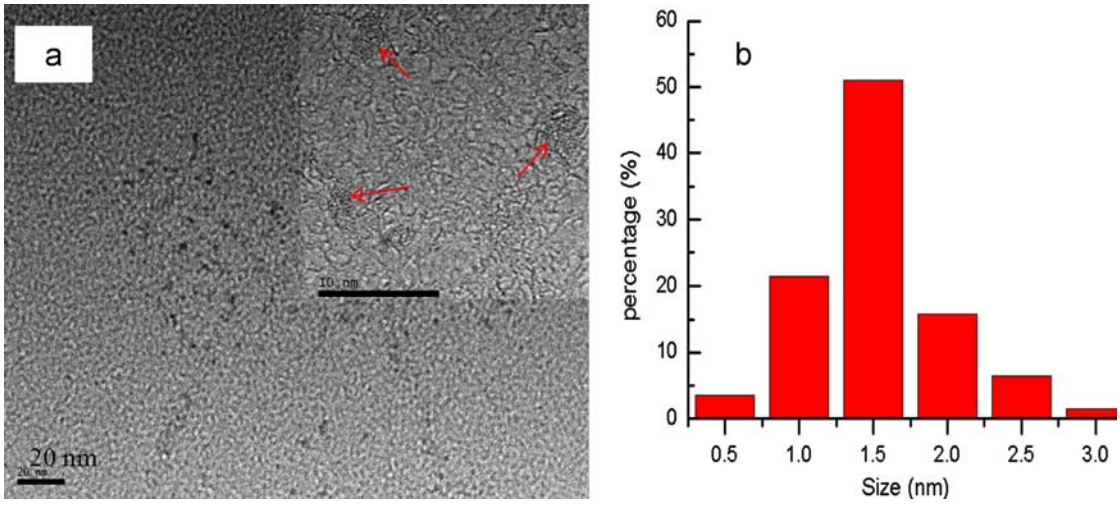


Fig. 2. (a) TEM image of CDs (the bar was 20 nm, inset: a HRTEM image of CDs and the bar was 10 nm) and (b) the size distributions of the CDs measured by TEM. About 140 CDs were measured and the average diameter was 1.5 nm.

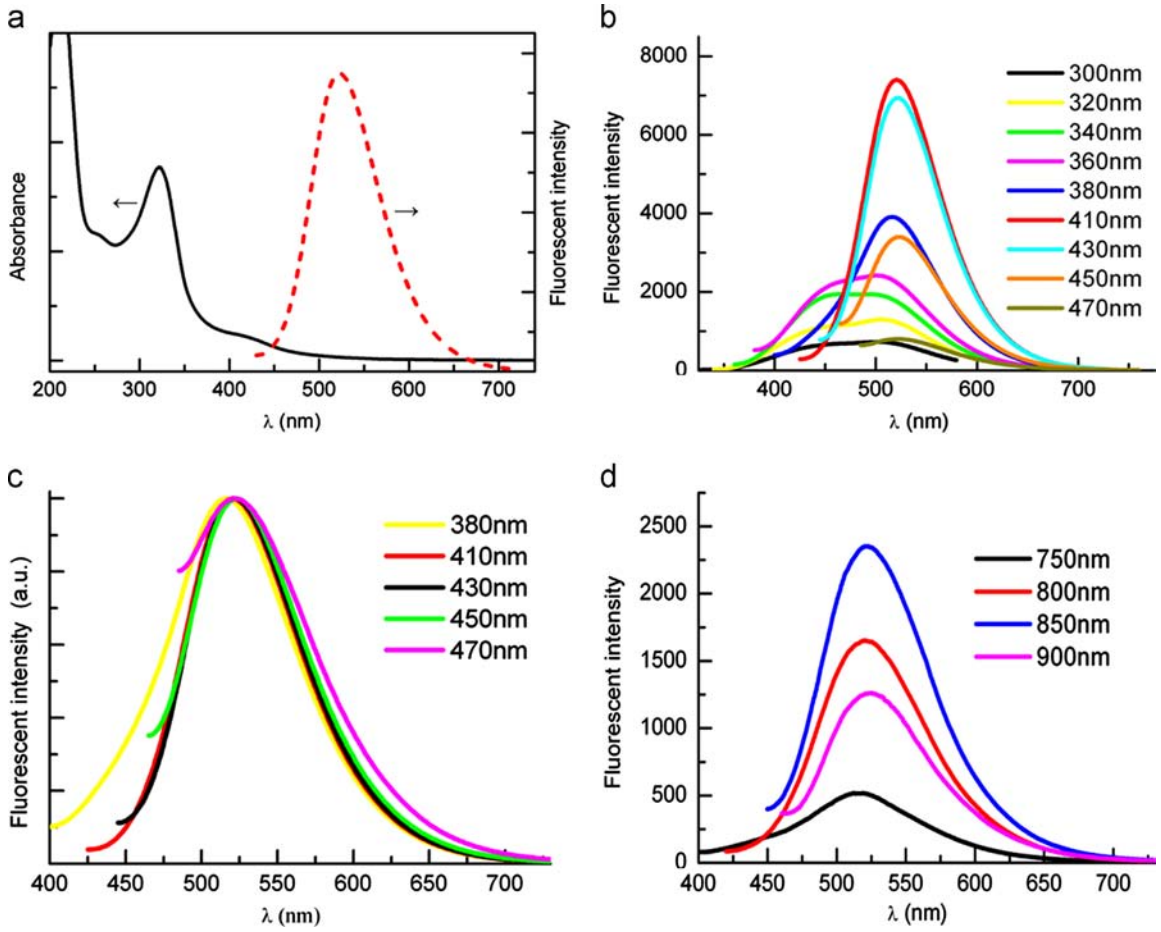


Fig. 3. (a) Typical absorption and photoluminescence emission spectra of the CDs. (b) Emission spectra of the CDs at different excitation wave-lengths as indicated. (c) Normalized emission spectra of the CDs at the excitation wavelengths as indicated. (d) Up-conversion fluorescent of the CDs at different excitation wavelengths as indicated.

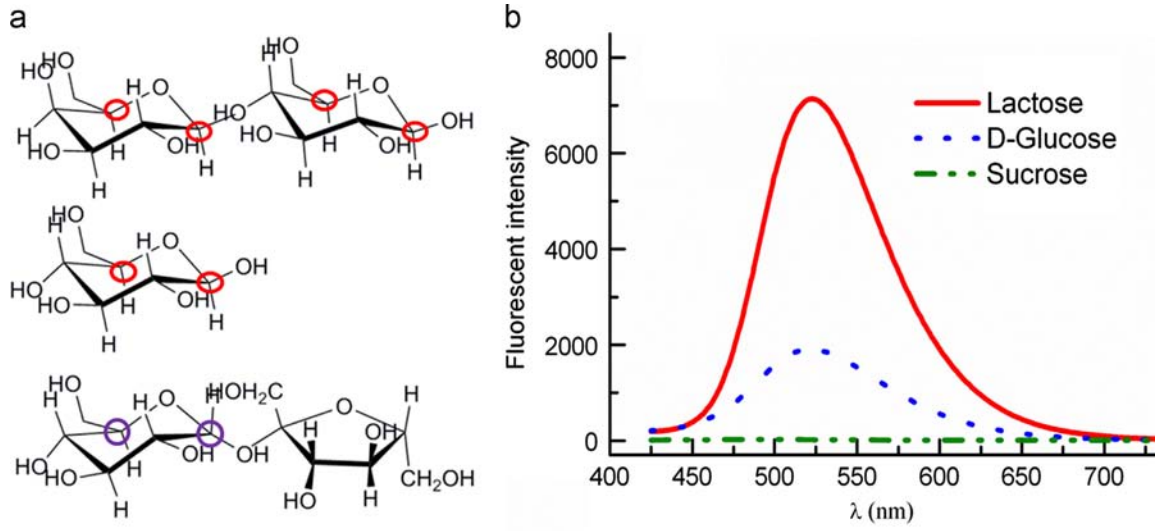


Fig. 4. (a) Structure of carbon sources (up to down was lactose, D-glucose and sucrose, respectively) and (b) the fluorescence properties of the products prepared by three carbon sources refluxing with Tris.

like below. First, unlike lactose with two relatively stable rings, glucose is partly a chain structure in aqueous solution, which was unfit for carbonization to form regular carbon core. Second, as a monosaccharide, glucose changes into mannose and fructose partly in alkalescence condition by epimerization [38], while they are unsuitable to be passivated by Tris according to their structures. This may make the corresponding quantum yield of CDs from glucose much lower than that from lactose.

Likely, we tried several small molecular organic compounds as surface passivation agents, including Tris, diethylene glycol, PEG_{200} [39], diethanolamine [17] and 2-(2-aminoethoxy) ethanol [21]. As seen from Table 2, the fluorescent carbon dots were successfully

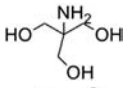
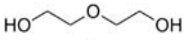
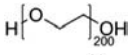
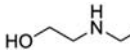
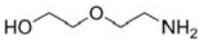
synthesized with Tris, diethanolamine and 2-(2-aminoethoxy) ethanol. On the contrary, there was no luminescence when passivated with diethylene glycol or PEG_{200}. Considering the structure of these compounds, we suppose that the introduction of amino group (or secondary amines) has a significant effect on the synthesis process. It means the nitrogen element played a key role in generating strong fluorescence, especially the amino group. The reasons why the adding of Tris enhanced the fluorescence greatly may be considered in two causes: first, Tris is an alkali and it provided an alkaline condition which is propitious to form carbon core [40]; second, the amino group of Tris makes it a good surface passivation agent for CDs as shown in Fig. 1. The synthesis and the surface modification of the luminescent CDs were believed to occur simultaneously. In the control experiments, neither lactose nor Tris exhibited any detectable photoluminescence when they were refluxed separately.

The surface passivation agents affected not only the fluorescent intensity but also the emission wavelength. As shown in Table 2, the CDs passivated with diethanolamine and 2-(2-aminoethoxy) ethanol show blue fluorescence with a maximal emission wavelength at 495 nm.

Table 1
Comparison of carbon sources when using Tris as surface passivation agent.

Carbon sources	λ_{em} (nm)	QY (%)
Lactose	523	12.5
D-Glucose	523	8.6
Sucrose	–	0

Table 2
Comparison of surface passivation agents when using lactose as carbon source.

Materials	Structure	λ_{em} (nm)	QY (%)
Tris		523	12.5
Diethylene glycol		–	0
PEG_{200}		–	0
Diethanolamine		495	0.58
2-(2-amino-ethoxy) ethanol		495	7.9

3.4. Effects of refluxing time and former pH

The fluorescence was greatly enhanced with an increasing reflux time in the beginning and it turned to be relatively stable since 20 h. Then after 28 h, the QY of CDs decreased instead. This may be due to the aggregation of CDs particles.

We found that the pH of the original mix solution (named as former pH) affected the formation of CDs straightly. As shown in Fig. 5, the acidity made against the preparation process. When the solution was alkaline, the pH not only affected the fluorescent intensity of obtained carbon dots, but also changed its λ_{em} from 490 nm to 523 nm, namely from blue to green. It can be seen from Fig. 5 that when the former pH was 10.5, the fluorescence intensity was maximal. The pH of the original mixed solution was about 10.5 adjusted by ionization of Tris, therefore no additive was needed to adjust the former pH.

3.5. Effects of salt concentration and pH

After the synthesis process, the effect of salt on the as-obtained CDs was investigated (Fig. S4a). It showed that the CDs had a strong tolerance of salt concentration. The fluorescent intensity had no obvious change even when the salt concentration came up to 2.0 mol L^{-1}. The pH value of the solution also affects the photoluminescence of the CDs slightly. As shown in Fig. S4b, the CDs were stable from pH 3.5 to pH 9.5. These characteristics made CDs suitable to apply to complex matrix, biosensing, or bioimaging.

3.6. Fluorescence imaging

As shown in Fig. 6, the CDs were able to label the cytoplasm while the cell nucleus was not infiltrated significantly, which indicates that the CDs easily penetrated into the cell but did not enter the nucleus. However, the mechanism of CDs uptaken by cells still requires more investigations. It was suggested that endocytosis mechanism may be the most likely one.

3.7. The in vitro cytotoxicity study of the carbon dots

Fig. 7 presented cytotoxicity of the different concentrations of CDs (0–400 mg mL^{-1}) toward HeLa cells after incubation of 48 and 72 h, respectively. Our MTT assay suggests CDs do not cause

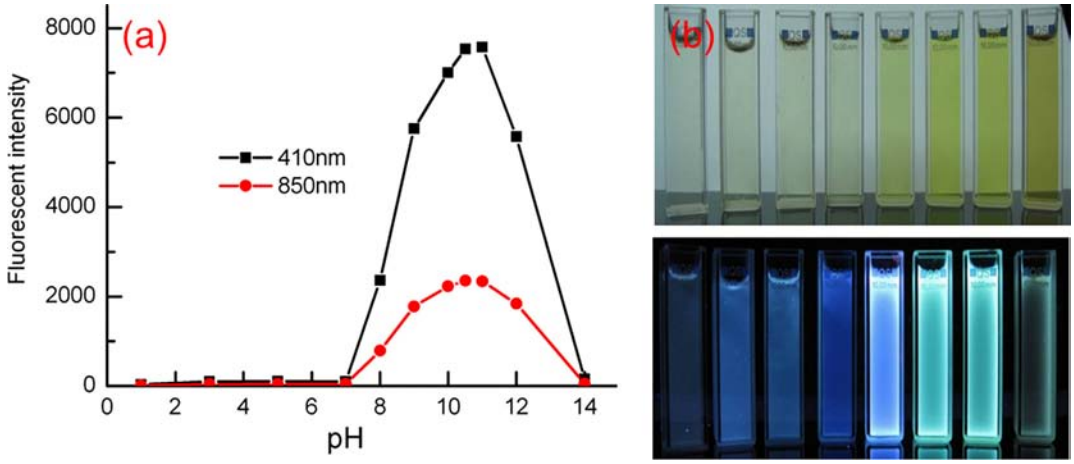


Fig. 5. (a) The influence of the former pH on fluorescence intensity of the CDs (emitted at 523 nm, excited at 410 or 850 nm). (b) Photographs of CDs under sunlight and 365 nm UV lamp respectively (the former pH values from left to right were 1.0, 3.0, 5.0, 7.0, 8.0, 10.0, 12.0, and 14.0).

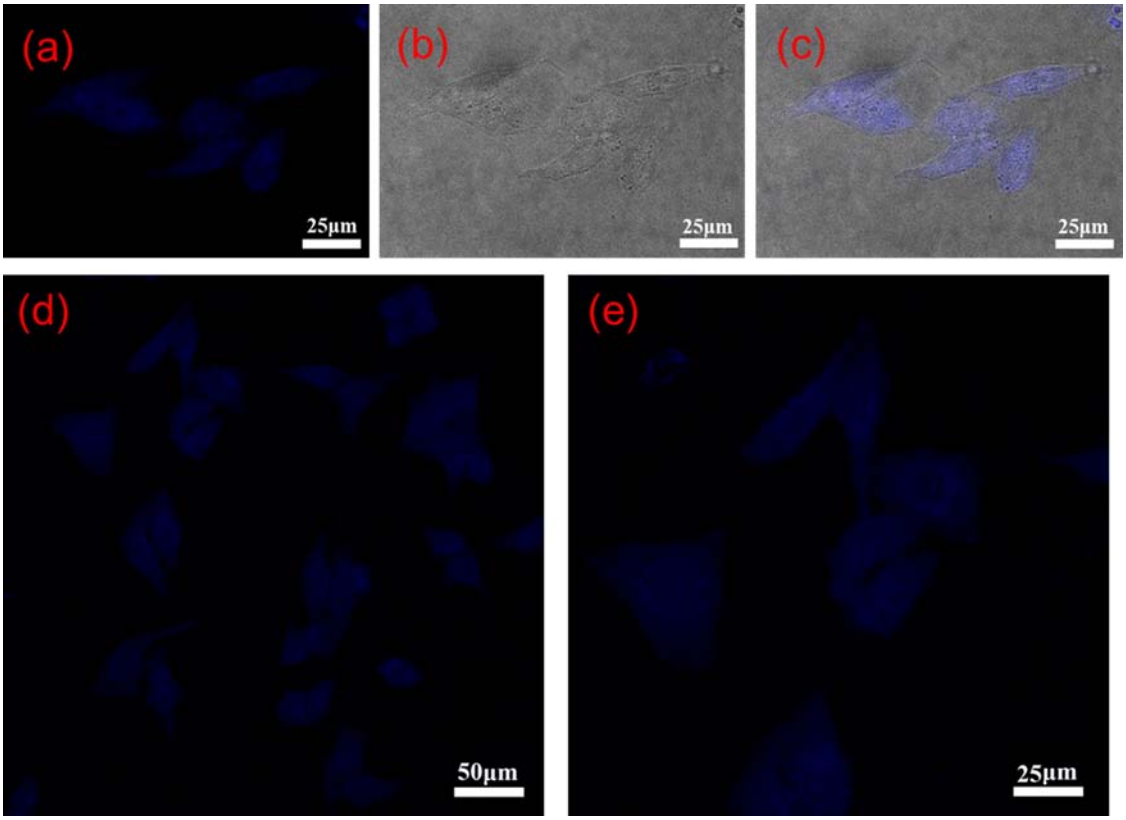


Fig. 6. (a, d, e) Confocal fluorescence images (λ_{ex}: 405 nm); (b) Bright-field microphotograph of HeLa cells incubated with 200 μg mL^{-1} of CDs for 4 h and (c) overlay image of (a) and (b).

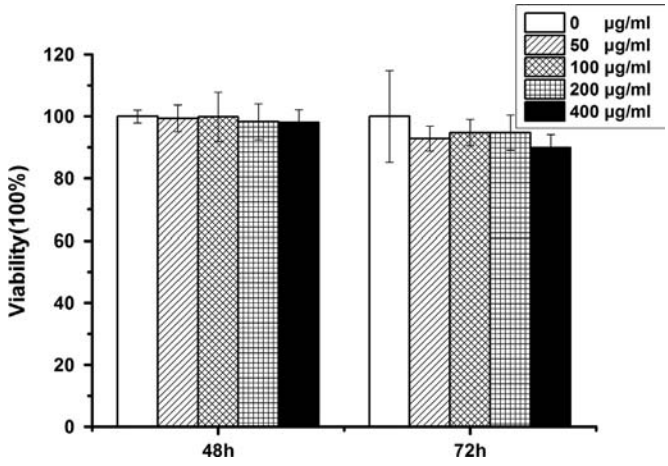


Fig. 7. Effects of carbon dots with different concentrations on the viability of HeLa cells at 48 and 72 h, as measured by MTT assay. Dates are represented as Mean ± SD.

significant cytotoxicity. However, the maximum concentration investigated was much higher than necessary for bioimaging studies and the exposure times are much longer, which suggests that CDs pose low toxicity effects at useful concentrations for bioimaging.

4. Conclusions

In summary, we synthesized water-soluble fluorescent CDs by the hydrothermal method using a common carbon resource. The nanoparticles were stable for several months under ambient conditions, and they can exhibit excellent photoluminescence and up-conversion fluorescence. The CDs were successfully applied to bioimaging of HeLa cells and the MTT assay showed their low cytotoxicity. The other point of the CDs was that they contained abundant hydroxyl groups on their surface, which made them convenient to couple with other groups or substance and easy to apply to biolabeling, biomedical or other area.

Acknowledgment

This work was supported by the National Basic Research Program of China (Nos. 2011CB707703 and 2012CB910601), the National Natural Science Foundation of China (Nos. 21075069 and 21275078), and the Tianjin Natural Science Foundation (No. 11JCZDJC21700).

Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.talanta.2013.09.003.

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