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A green heterogeneous synthesis of N-doped carbon dots and their photoluminescence applications with solid and aqueous states

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Compared to traditional semiconductor quantum dots (QDs) and organic dyes, photoluminescent carbon dots (CDs) are superior in terms of high aqueous solubility, robust chemical inertness, easy functionalization, high resistance to photobleaching, low toxicity and good biocompatibility. Herein, a green, large-scale and high-output heterogeneous synthesis of N-doped CDs was developed by calcium citrate and urea under microwave irradiation, without using any capping agent. The obtained N-doped CDs with uniform size distribution possess good aqueous solubility, yellowish-green fluorescence in solid and aqueous states. These unique luminescence properties of N-doped CDs inspire new thoughts on the applications of fluorescent powders, fluorescent ink, growth of fluorescent bean sprouts, and fingerprint detection.

1 Introduction

In recent years, carbon dots (CDs) are inspiring intensive research interests due to their high aqueous solubility, chemical inertness, low toxicity, easy functionalization and resistance to photobleaching.[1] Therefore, CDs provide a wide variety of promising applications in bio-imaging,[2-4] photocatalysis,[5,6] optoelectronic devices,[7,8] drug and gene delivery,[9,10] and chemical sensor and biosensor.[11,12] Synthetic methods of CDs with adjustable sizes can be generally classified into two main groups: chemical and physical methods. Chemical methods include electrochemical synthesis,[13] combustion/thermal/hydrothermal/acidic oxygen,[14-17] supported methods,[18] microwave/ultrasonic,[19,20] and so on. Physical methods involve arc discharge,[21] laser ablation/passivation,[22,23] and plasma treatment.[24]

Among these methods, microwave method draws great attention due to certain benefits of microwave heating, such as faster reaction rate, milder reaction conditions, higher chemical yield, and lower energy usage. Zhu et al.[25] presented an economical and facile microwave pyrolysis approach to synthesize CDs with different amounts of poly (ethylene glycol) and saccharide under 500 W for 2 ~ 10 min. As reaction time increased, the colour of the solution changed from colourless to yellow and finally to dark brown, which implied the formation of CDs. Zhai et al.[26] reported a method using citric acid as carbon source and amine molecules, including 1,2-ethylenediamine, diethylamine, triethylamine and 1,4-butanediamine as the passivation agents to synthesize N-doped CDs. The primary amine molecules had been confirmed to serve dual roles as N-doped precursors and surface passivation agents. Jiang et al.[27] developed a general strategy for the production of N-doped CDs by microwave irradiation of amino acids in the presence of acid or alkali. These N-doped CDs could effectively enhance the ultra-weak chemiluminecence in the reaction of $NaIO_4$ with H_2O_2. Salinas-Castillo et al.[28] reported a one-step microwave method to prepare N-doped CDs by pyrolysis of citric acid in the presence of polyethylenimine at low temperature. The as-synthesized N-doped CDs with down and upconversion luminescence properties could selectively and sensitively detect Cu^{2+}. Hou et al.[29] proposed that using triammonium citrate or citrate acid with soluble phosphate could synthesize CDs powders under microwave condition.

Recently, Zhou *et al.*[30] synthesized fluorescent carbon nitride dots through a low-temperature solid-phase condition with sodium citrate and urea as the precursors. However, there is no report about insoluble solid heterogeneous synthesis of CDs under microwave irradiation.[31] In addition, in the past research, the performance of CDs-based solid-state luminescent devices is not satisfactory because strong fluorescence quenching occurs in dry and aggregate states. Our synthesized N-doped CDs can emit photoluminescence at both solid and aqueous states. Besides, these as-synthesized N-doped CDs with uniform particle size, good aqueous solubility, yellowish-green fluorescence have been applied into fluorescent powders, fluorescent ink, growth of fluorescent bean sprouts, and fingerprint detection.

2 Experimental

2.1 Chemicals

Calcium citrate, sodium citrate, potassium citrate, magnesium citrate, copper citrate, and iron citrate were analytical-reagent grade and purchased from Aladdin Chemistry Co. Ltd (Shanghai, China). Urea was analytical-reagent grade and purchased from Sinopharm Chemical Reagent Co. Ltd (Shanghai, China). Deionized water with a resistivity of 18.1 MΩ·cm was used for all experiments.

2.2 Synthesis of N-doped CDs

Calcium citrate (3 g, 5.3 mmol) and urea (3 g, 50.0 mmol) were added in 10 mL deionized water and stirred to form a suspension liquid. It is worth noting that calcium citrate is not dissolved in water so that the temperature is decreased after mixing the suspension. The heterogeneous solution was then heated in a domestic microwave oven (800 W) for 5 min, the suspension solution was changed from turbid liquid to yellow clustered solid, indicating the formation of N-doped CDs. The solid was then heated at 60 °C for 1 h. A turbid liquid of crude N-doped CDs was centrifuged at 8270 *g* for 30 min to remove unreacted calcium citrate. The obtained solution was concentrated, and then transferred to a silica gel column. Next, the solution was eluted with methanol and dichloromethane mixtures from 1:2 to 1:1 (v:v) to obtain bright yellowish-green fluorescent N-doped CDs. Other metal citrates, such as sodium citrate, potassium citrate, magnesium citrate, copper citrate, and iron citrate, were used with the same condition in control experiments with urea.

2.3 Effects of different concentration of N-doped CDs on the growth of normal green beans

Green grams were sowed in 7.0 cm diameter round culture dishes, and covered with pure water for the control experiments and aqueous solution of different concentration of N-doped CDs (0.1, 0.5, 1.0, 1.5, 2.0, 2.5, 5.0, and 10.0 mg/mL), respectively. Then, the dishes were placed for different periods of time without lids so as to make sure the sufficient oxygen supply. During the growth, appropriate water was supplemented to the dishes to keep the fixed volume of solution to avoid evaporation. The average lengths of 29 bean sprouts were measured, and their growth situations were photographed.

2.4 Growth and photoluminescence detection of bean sprouts

For comparison, green beans were added into 1.5 mg/mL N-doped CDs solution (our method), 0.1 mg/mL CdTe QDs solution,[32] 1.5 mg/mL N-doped CDs solution (citric acid, urea),[19] and pure water. Keep bean sprouts wet at 25 °C for 96 h and take photos to observe the growth of bean sprouts every 24 h. The experimental details were as above. The photoluminescent phenomenon was detected by 365 nm UV beam.

2.5 Preparation of fluorescent powders

5 mL N-doped CDs solution prepared by our method was added into 5 g commercial silica gel, making silica gel completely soaking. The solution was evaporated from this mixture to obtain dry fluorescent powders.

2.6 Characterization

The morphologies of the samples were observed by transmission electron microscope (TEM, JEM-2100, JEOL, Japan) and atomic force microscopy (AFM, Multimode Nanoscope, DI, USA). The photoluminescent (PL) and photoluminescence emission (PLE) spectra were performed through a fluorescent spectrophotometer (F-4600, Hitachi, Japan). The ultraviolet-visible (UV-Vis) absorption spectrum was recorded by a UV-Vis-NIR spectrophotometer (Lambda 950, Perkin-Elmer, USA). Fourier transform infrared spectroscopy (FT-IR) was recorded on a VERTEC 70, Bruker, Germany spectrometer with room temperature deuterated L-alanine-doped triglycine sulfate (RT-DLaTGS) as a detector. The fluorescence microscopy images were performed with inverted luminescence microscope (Olympus IX71, Japan). The light source for fluorescence microscopy observation was a halogen lamp or a mercury lamp with a fluorescent filter cube. Raman spectroscopy was

characterized using Bruker Senterra dispersive Raman microscopy with laser wavelength at 633 nm. X-ray photoelectron spectra (XPS) were acquired with a Japan Kratos Axis UltraDLD spectrometer using a monochromatic Al Kα source (1486.6 eV). ^{1}H-NMR was recorded on a MERCURYplus 400 instrument (Varian, Inc., USA) at 400 MHz and tetramethylsilane was used as an internal standard.

3 Results and discussion

N-doped CDs were prepared through a one-pot microwave heterogeneous process of calcium citrate (insoluble solid) and urea at 800 W for 5 min. The role of calcium citrate is the carbon source of CDs. Urea is selected as the nitrogen source due to its low-cost, abundance, and nitrogen-rich nature. It is violently decomposed with water evaporation during the reaction process. Citric acid and urea were also used to synthesize N-doped CDs,[19] but these synthesized N-doped CDs emitted no fluorescence in solid state. The products between sodium citrate, potassium citrate, magnesium citrate (insoluble solid), copper citrate (insoluble solid), iron citrate (insoluble solid) with urea under microwave irradiation were seen in Figs. S1 and S2. The reactions of soluble solids like sodium citrate and potassium citrate with urea cannot obtain fluorescent CDs due to easily complete carbonization. Due to quenching effect of Cu^{2+} [24] and Fe^{3+} [33], the reactions of copper citrate (insoluble solid) and iron citrate (insoluble solid) with urea also cannot obtain fluorescent CDs. However, insoluble solids magnesium citrate and calcium citrate with urea can obtain fluorescent CDs possibly due to suitable metal elements, respectively. The blue fluorescence from magnesium citrate and urea may be attributed to a surface state in which urea groups formed intermolecular H-bonds, while the yellowish-green fluorescence from calcium citrate and urea may be ascribed to a surface state in which urea groups formed intramolecular H-bonds.[34] The aqueous solution states under daylight and 365 nm UV beam of these reactions were shown in Fig. S3.

The impurities, such as precursor residues and resulting by products were removed by centrifugation and column chromatography. The resultant N-doped CDs were evaporated into solid states and then dispersed into water for further characterization and applications. It is found that it is remarkably stable to repeatedly disperse the dry powders into water without any aggregation, which is significant for preservation and transportation. The yield of as-prepared N-doped CDs is 28 %. Fig. 1 gives the photos of calcium citrate and N-doped CDs powders prepared from calcium citrate with urea under daylight and a 365 nm UV beam, respectively, which suggests that N-doped CDs possess good fluorescence property in solid state.
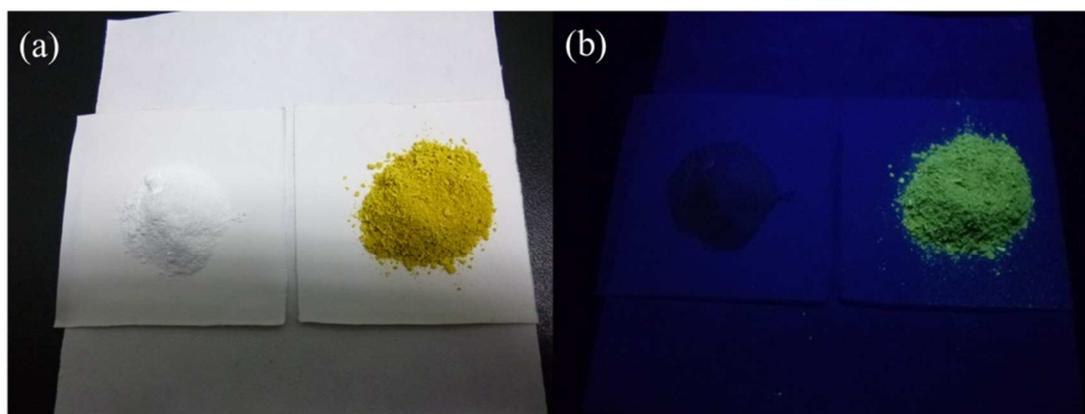

Fig. 1 The photos of calcium citrate and N-doped CDs: (a) under visible light and (b) under a 365 nm UV beam.

Fig. 2(a) and (b) shows a typical TEM image and particle size distribution by counting the average sizes of 200 nanoparticles. The Gaussian fitting curve reveals that the average size of N-doped CDs is 2.18 ± 0.36 nm. N-doped CDs are uniform in size and present a nearly spherical shape. Fig. 2(c) and (d) shows AFM image and height profiles of N-doped CDs. The height of N-doped CDs is approximately 2.5 nm, which is slightly higher than the size of N-doped CDs in TEM image due to the environmental conditions such as relative humidity in AFM measurement.[35]
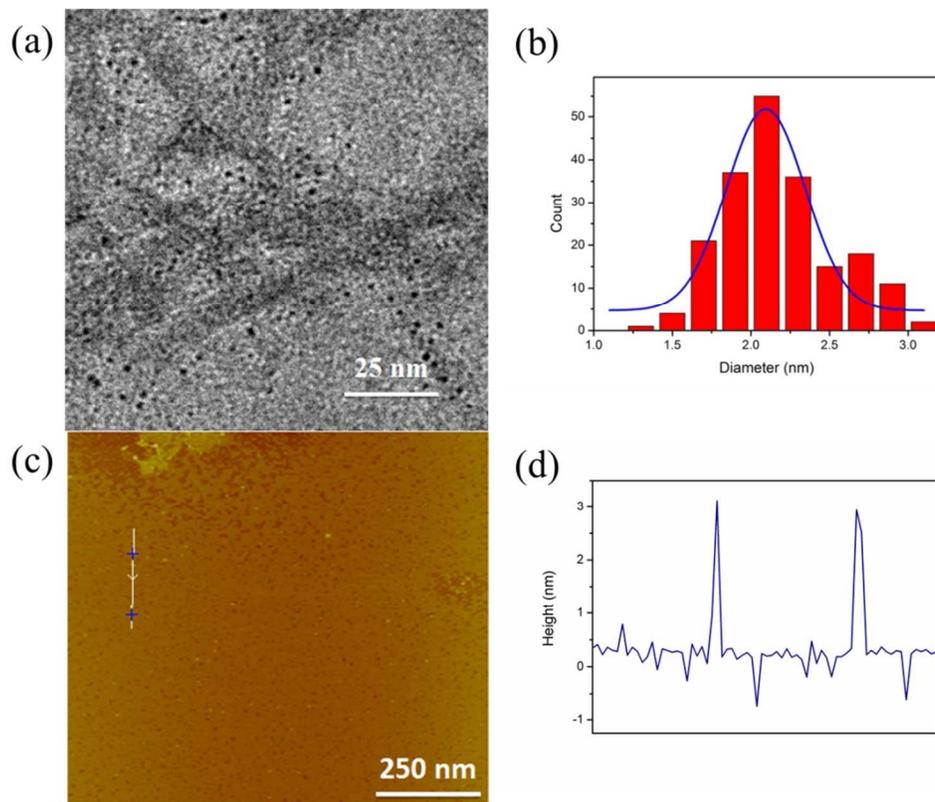
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Fig. 2 (a) TEM image and (b) particle size distribution of N-doped CDs; (c) AFM image and (d) height profile of N-doped CDs.

Since neither calcium citrate nor urea has absorption in UV and the visible range, the absorption is attributed to the N-doped CDs. Fig. 3(a) shows the dilute aqueous solution of N-doped CDs has a broad absorption spectrum with peaks centered at 217, 249, and 272 nm which are ascribed to carbonic core center, and the absorption peak centered at 406 nm can be attributed to surface/molecule center. These absorption peaks indicate extended conjugations in the N-doped CD structures.[19] The high energy tail in the visible region of the absorption spectrum of N-doped CDs is attributed to Mie scattering which is caused by nanosized particles.[36]

From the fundamental and application viewpoints, PL is one of the most fascinated features of N-doped CDs. Fig. 3(b) shows PLE spectrum peak at 272 nm, and 398 nm under excitation of 520 nm. These two peaks at 272 and 398 nm are corresponding to those of UV-Vis absorption spectrum. As shown in Fig. 3(c), the 398 nm peak stands for the strong emission peak of PL emission. When the excitation wavelength is changed from 300 to 390 nm, the fluorescence emission peak is slightly red-shifted. When the excitation wavelength is changed from 390 to 510 nm, the fluorescence emission peak at 520 nm remains unchanged. The excitation-independent PL behaviour is considered to be related to less surface defects and more uniform size of N-doped CDs, which is consistent with TEM and AFM observations. The synergistic effect of the carbon core and the surface/molecule state contributed to the PL of N-doped CDs. As described in the supporting information, the fluorescence quantum yield of N-doped CDs was measured to be about 10.1 % with quinine sulfate in 0.1 M sulphuric acid solution (quantum yield 54 %) as a

reference.[37] This QY value is comparable to previous reports.[25,38,39]

The structure and composition of N-doped CDs were characterized by FT-IR spectroscopy. As shown in Fig. 3(d), the synthesized N-doped CDs show main absorption bands of O-H stretching vibration at 3435 cm^{-1} and the amide bond from C=O stretching at 1626 cm^{-1} in the spectrum. The weak peaks at 2925 and 2855 cm^{-1} are related to the C-H bond stretching vibrations. The characteristic stretch band of the amine III C-N bond is at 1454 cm^{-1}, which is contributed to urea. The bending vibration of

C-O bond and stretching peak of C-O-C bond appear at 1390 and 1093 cm^{-1}, respectively.[40] These functional groups improve the hydrophilcity and stability of the N-doped CDs in aqueous system. ^{1}H-NMR spectrum of N-doped CDs (Fig. S4) is composed of sp[2] carbon with 6.9 and 8.7 ppm and sp[3] carbon with 3.5 ppm. The peak at 5.7 ppm is CH of propylene group,[41] The active hydrogen is situated at 11.3 ppm. Attempt to obtain Raman spectrum (Fig. S5) is unsuccessful due to the intense fluorescence of N-doped CDs, resulting in covering the characteristics of the Raman signal.[15,42,43]
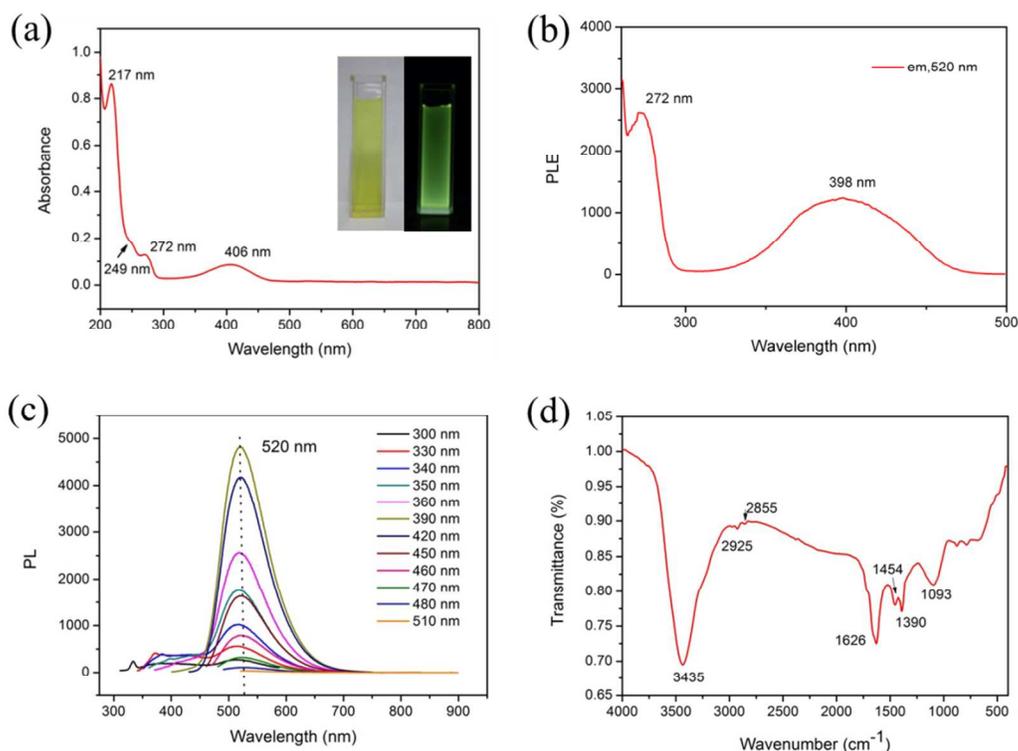

Fig. 3 (a) UV-Vis absorption spectrum of N-doped CDs, inset are photos of N-doped CDs solution under sunlight (left) and irradiated by a 365 nm UV beam (right); (b) PLE spectrum of N-doped CDs; (c) PL spectra recorded for progressively longer excitation wavelengths from 300 to 510 nm; (d) FT-IR spectrum of N-doped CDs.

XPS measurements were performed to indicate the surface element analysis of N-doped CDs. The XPS spectrum shown in Fig. 4(a) clearly reveals that carbon, nitrogen and oxygen elements are present at the surface of N-doped CDs. In the expanded XPS spectra, the C1s peaks at 284.0, 285.0, 286.1, and 289.0 eV shown in Fig. 4 (b) can be assigned to carbon in the form of C-C (sp[3])/C=C (sp[2]), C-H (sp[3]), C-O or C-N (sp[3]), and O-C=O (sp[2])/C=N (sp[2]), respectively.[43,44] The N1s peaks at 399.2 and 400.2 eV shown in Fig. 4(c) indicate that nitrogen exists

mostly in the form of C-N-C (sp[3]) and (C)$_3$-N (sp[3]), respectively.[43] These results prove that the synthesized CDs are nitrogen-doped CDs. The O1s peaks at 531.0 and 532.0 eV shown in Fig. 4(d) are associated with C=O quinone type groups, and C-OH phenol groups and/or C-O-C ether groups.[45] The characterizations from FT-IR and XPS indicate that the surface of the as-synthesized N-CDs are functionalized by multiple oxygenated and nitrous groups. As shown in Table S1, 39.17 %

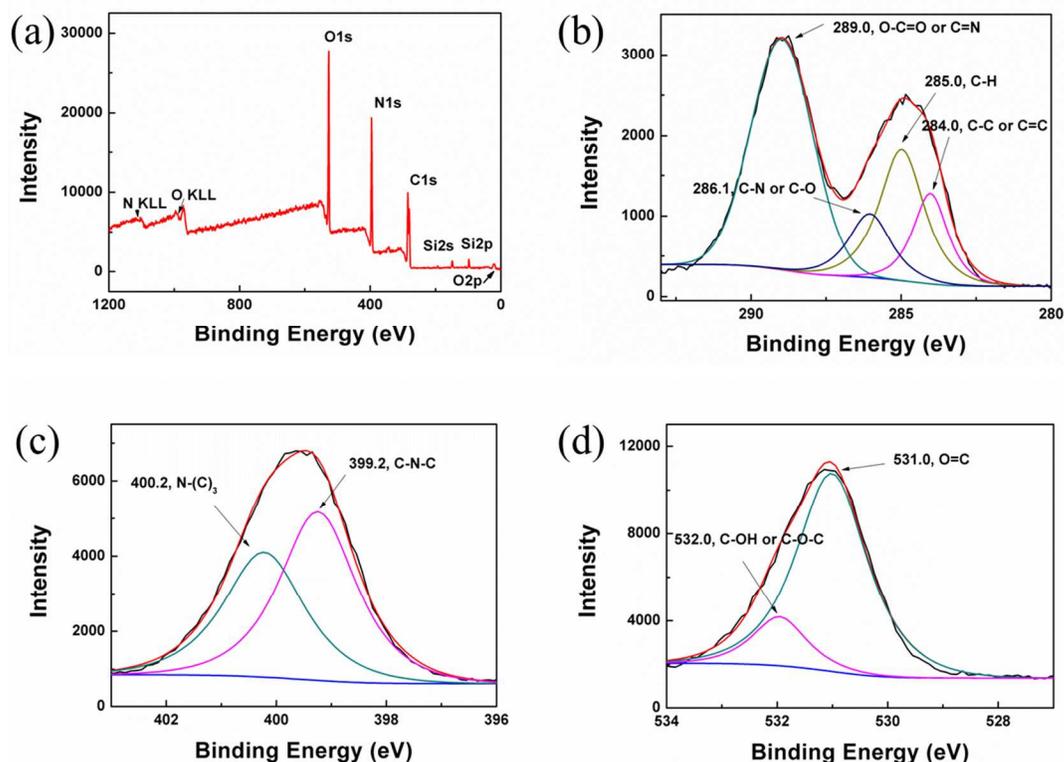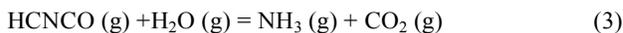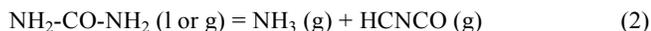of nitrogen and 30.08 % of carbon indicate that CDs are nitrogen- rich, and carbon-rich.[46]

Fig. 4 XPS survey scan of N-doped CDs. (a) XPS scanning spectra show three major peaks of carbon, nitrogen and oxygen. XPS high resolution survey scan of (b) C1s, (c) N1s and (d) O1s region of N-doped CDs.

As shown in Fig. 5, a possible mechanism for the formation of N-doped CDs was proposed by this method. Urea, as a nitrogen source, is an active substances under thermal treatment,[47,48] which is first decomposed at 180 °C and can produce a large amount of NH_3 through fast and efficient heating during microwave process.[30] The chemical equation is outline below: [49,50]

$$NH_2\text{-}CO\text{-}NH_2 \text{ (aq)} = NH_2\text{-}CO\text{-}NH_2 \text{ (l or g)} + x\ H_2O \text{ (g)} \qquad (1)$$

$$NH_2\text{-}CO\text{-}NH_2 \text{ (l or g)} = NH_3 \text{ (g)} + HCNCO \text{ (g)} \qquad (2)$$

$$HCNCO \text{ (g)} + H_2O \text{ (g)} = NH_3 \text{ (g)} + CO_2 \text{ (g)} \qquad (3)$$

It also accelerates the decomposition of calcium citrate and prevents non-uniform nucleation growth. Calcium citrate functions as the carbon source and provides negative surface functional groups such as carboxyl and hydroxyl groups for the N-doped CDs. A heterogeneous solution might undergo thermal carbonization of the precursors and lead to nucleation. Finally the nuclei grows by the diffusion of other molecules towards surfaces of nanoparticles.[29]
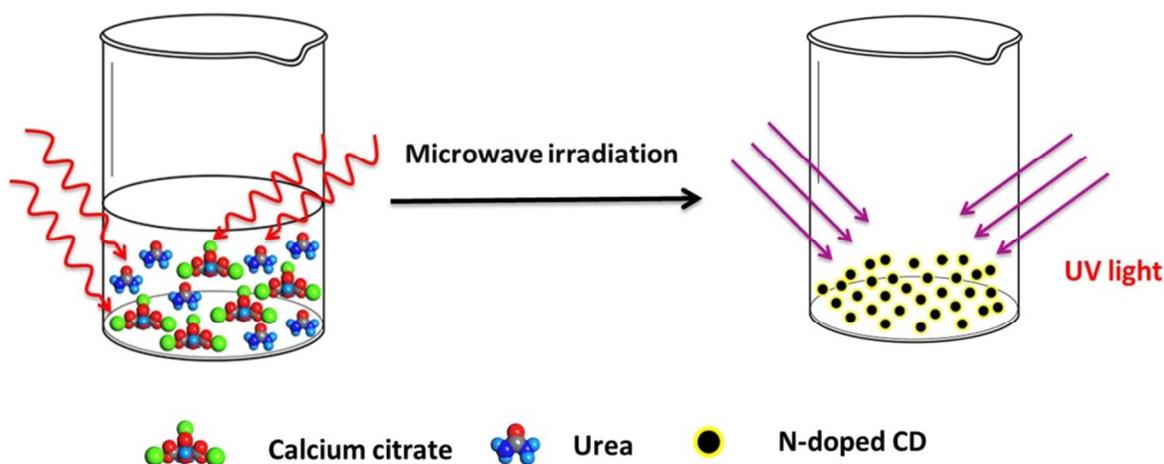
Fig. 5 Schematic diagram of the formation mechanism of N-doped CDs.

Traditionally, a thorough PL quenching was observed in powder samples, which may be attributed to re-absorption effect, electronic quenching at the excited state, or an induced photothermal effect. The fluorescence is strongly quenched when the aqueous solutions of CDs are deposited on glass, metal, silicon, or plastic substrates owing to the formation of aggregates.[19] However, the as-synthesized N-doped CDs shown in Figs. 1, S1, S2 and S3 can emit fluorescence in solid and aqueous states. Thus, it can be applied in imaging of lens paper and grass leaf. Fig. 6 shows the blue, green and red fluorescence images could be obtained on lens paper and grass leaf because of fluorescence of N-doped CDs. This phenomenon is essential for identifying N-doped CDs.
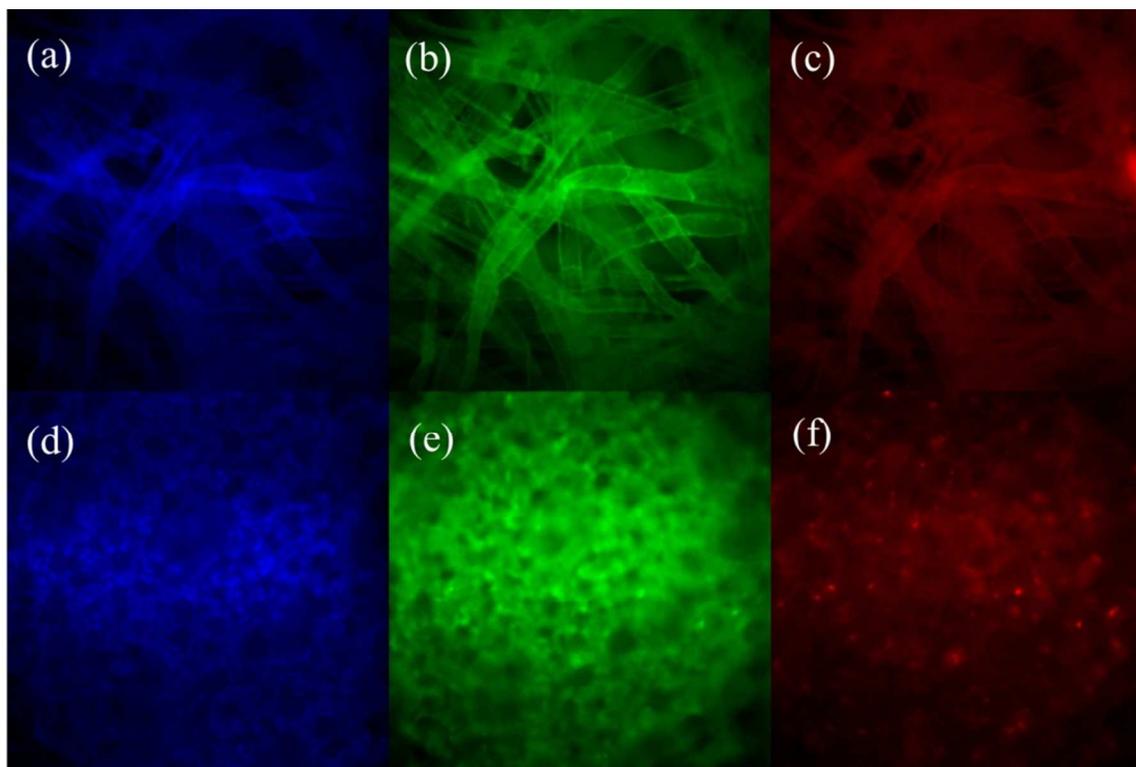

Fig. 6 Fluorescence images on lens paper composed from N-doped CDs aqueous solutions (a) exposure time 20 ms, exciter filter Ex 330-385 nm, Em 420 nm; (b) exposure time 150 ms, exciter filter Ex 450-480 nm, Em 515 nm; (c) exposure time 3000 ms, exciter filter Ex 510-550 nm, Em 590 nm;

fluorescence images on grass leaf composed from N-doped CDs aqueous solutions (d) exposure time 50 ms, exciter filter Ex 330-385 nm, Em 420 nm; (e) exposure time 2500 ms, exciter filter Ex 450-480 nm, Em 515 nm; (f) exposure time 2500 ms, exciter filter Ex 510-550 nm, Em 590 nm.

Toxicity study of N-doped CDs was performed with plants. Green beans grew in N-doped CDs solution (our method), N-doped CDs solution (citric acid and urea), [19] CdTe QDs solution,[32] and pure water shown in Figs. S6-S9. The size of N-doped CDs from citric acid and urea are approximately 1.76 nm. The average size of CdTe CDs is 3.5 nm.[32] These small nanoparticles can easily enter into the cytoderm of bean sprouts. In CdTe QDs solution, bean sprouts are pathological as a result of the toxicity of CdTe QDs.[51]

As shown in Fig. 7, the fluorescence property of the bean sprouts indicates that N-doped CDs could permeate throughout the plant cells with good biocompatibility, but they are nontoxic and do not hinder plant growth.

As is known, N-doped CDs in a higher concentration would have an obvious impact on human or animal cells. We explore the concentration range for normal growth of green beans (See Figs. S10-S14). It can be seen that an obvious dose-dependent effect after 96 h growth due to high osmotic pressure (See Fig. S15).
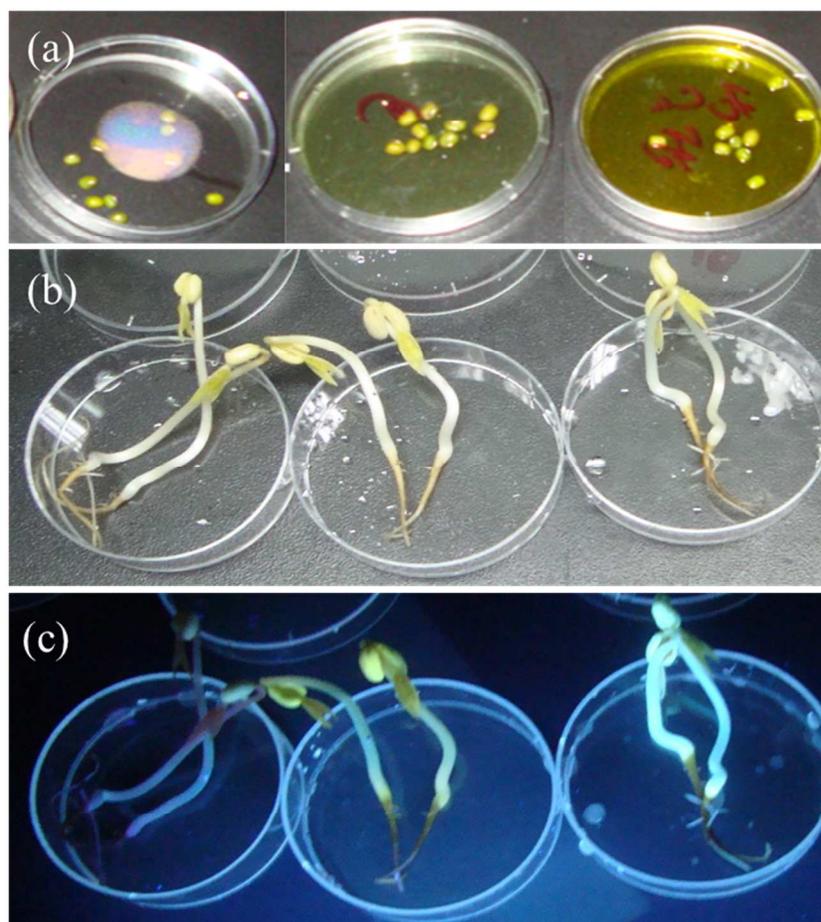

Fig. 7 (a) Green beans were added into solution; Bean sprouts photos under (b) daylight and (c) 365 nm UV beam after a few days growth. From left to right: pure water, N-doped CDs solution (our method), N-doped CDs solution (citric acid and urea).[19]

As shown in Fig. 8(a) and (b), the non-fluorescent silica powder was changed into fluorescent-response powder just after adsorption of N-doped CDs. In addition, the fluorescent powders can be preserved for several months without significant fluorescent change.[52] N-doped CDs-based fluorescent fingerprint on filter paper was shown in Fig. 8(c) and (d). The water-soluble N-doped CD-based fluorescent ink can replace traditional inks to form clear, adelomorphic, long-time, and yellowish-green fluorescent fingerprints and would not contaminate fingers, which can be easily washed off with water.[19]
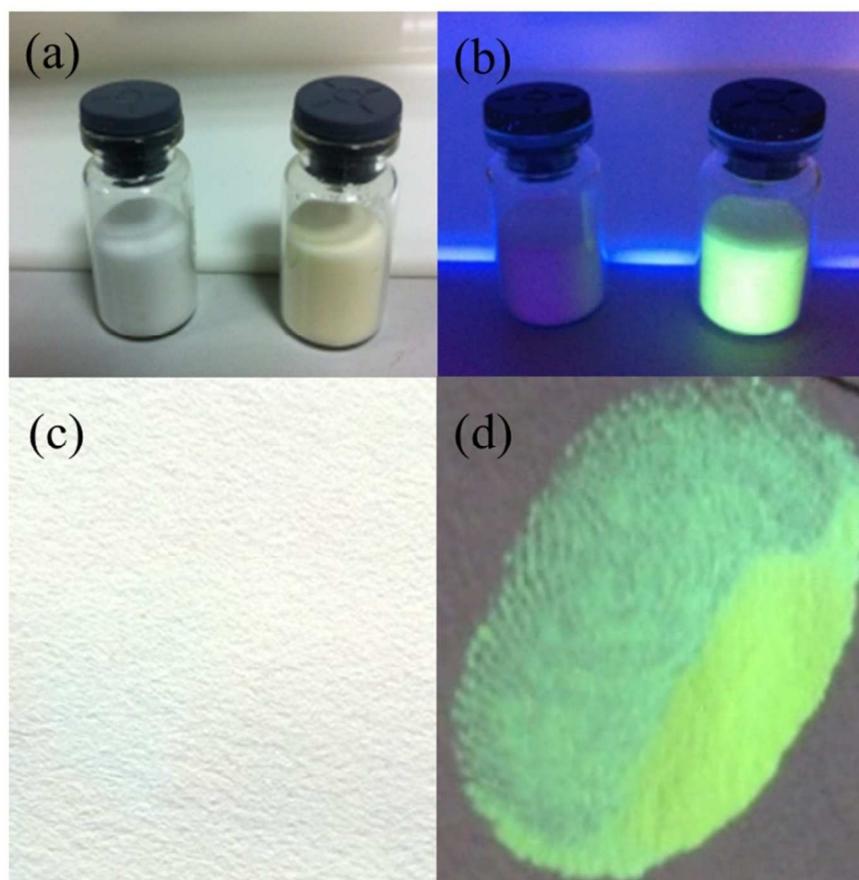
Fig. 8 (a) Daylight and (b) 365 nm UV beam photo of silica gel (left) and silica gel contain N-doped CDs (right); (c) daylight and (d) 365 nm UV beam of N-doped CDs pinned on filter paper.

4 Conclusions

A simple, large-scale, green, and cost-effective heterogeneous synthesis of photoluminescent N-doped CDs by calcium citrate (insoluble solid) and urea has been reported. We have demonstrated a straightforward approach to produce N-doped CDs under microwave irradiation. With this route, the formation of the N-doped CDs was carried out without surface passivation, resulting in yellowish-green fluorescence. The unique photoluminescence properties of the N-doped CDs cause new thoughts on the application of fluorescent powders, fluorescent ink, growth of fluorescent bean sprouts, and fingerprint detection. The low cost, biocompatibility, and low-toxicity of N-doped CDs and their distinct PL properties indicate that N-doped CDs could potentially be synthesized on industrial scale and could be used for an enormous range of possible applications.

Acknowledgements

Notes and references

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