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Presence of photoluminescent carbon dots in Nescafe® original instant coffee: Applications to bioimaging

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ABSTRACT

The presence of the carbon dots (C-dots) in food is a hotly debated topic and our knowledge about the presence and the use of carbon dots (C-dots) in food is still in its infancy. We report the finding of the presence of photoluminescent (PL) C-dots in commercial Nescafe instant coffee. TEM analysis reveals that the extracted C-dots have an average size of 4.4 nm. They were well-dispersed in water and strongly photoluminescent under the excitation of ultra-violet light with a quantum yield (QY) about 5.5%, which were also found to possess clear upconversion PL properties. X-ray photoelectron spectroscopy characterization demonstrates that the C-dots contain C, O and N three elements with the relative contents *ca.* 30.1, 62.2 and 7.8%. The X-ray diffraction (XRD) analysis indicates that the C-dots are amorphous. Fourier-transform infrared (FTIR) spectra were employed to characterize the surface groups of the C-dots. The C-dots show a pH independent behavior by varying the pH value from 2 to 11. The cytotoxicity study revealed that the C-dots did not cause any toxicity to cells at a concentration as high as 20 mg/mL. The C-dots have been directly applied in cells and fish imaging, which suggested that the C-dots present in commercial coffee may have more potential biological applications.

1. Introduction

In recent years carbon nanomaterials, such as fullerenes, carbon nanotubes, graphene and carbon dots(C-dots), have attracted significant attention because of their unique electronic, mechanical, thermal, optical and chemical properties [1,2]. Among them, C-dots are a new class of quantum dot (QD)-like photoluminescent nanomaterials which are chemically stable, environmentally and biologically compatible in contrast to the traditional semiconductor QDs [3]. The wavelength-tuneable emission property has made them promising candidates as new 'nanolights' for biological applications. Unlike the semiconductor QDs essentially contain heavy metals which have known toxicity and are environmentally hazardous; the C-dots are more safe and non-toxic both in cell and animal level, suggesting their good biocompatibility for biomedical applications [3,4]. The syntheses, fluorescent properties and evaluations for sensing, imaging and photochemical catalysis of carbon dots have been intensively investigated worldwide since the original report in 2006 [5–8]. The photoluminescent C-dots are considered very useful as high-performance yet nontoxic fluorescence agents for optical bio-imaging in biomedical field [9,10].

Various synthetic methods have been developed for preparation of C-dots, such as the top-down methods of laser ablation [5] and electrochemical oxidation, [11] bottom-up methods of microwave-assisted synthesis, [12,13] hydrothermal synthetic route [14] and combustion thermal oxidation [15]. However, all the synthetic methods suffer to some degree from drawbacks such as harsh reaction conditions, tedious processes or toxicity starting materials. In this regard, the idea of searching for C-dots within regular food can overcome the above mentioned drawbacks. This prompted us to search for C-dots in food items that can potentially be used for biological applications. Some foods have been consumed by human for centuries, that are hardly considered as toxic. From this point, the concern of the origin and toxicity of the C-dots can be easily dispelled when they are used for biological applications.

Our knowledge about the presence and the use of carbon dots in food is still in its infancy. The presence of the C-dots within food is a hotly debated topic [16]. The discovery of the C-dots in food and evaluation of their potential biological applications is a hardly mentioned area. We have come across the photoluminescence (PL) of Nescafe Original instant coffee, in which we assumed the presence of the C-dots. This motivated us to analyze the components of the commercial coffee for the discovery of photoluminescent C-dots. In this paper, the presence of photoluminescent C-dots in instant coffee was reported and their photoluminescent properties were characterized originally. Further, the direct use of

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C-dots was evaluated for live cells and *in vivo* guppy fish imaging. Nevertheless, it is hard to find such photoluminescent nanomaterials in human drinks that intrinsically satisfy the criteria for bioimaging with strong PL and good biocompatibility, simultaneously. To the best of our knowledge, only one type of such C-dots has been reported in carbohydrate based food caramels, *viz*. bread, jaggery, sugar caramel, corn flakes and biscuits [16]. Thanks to their presence in human food, the C-dots in coffee have been consumed by human beings with no known toxicity and thus we believe that they may be preferred as fluorescent probes for biomedical applications.

2. Experimental section

2.1. Materials

Nescafe® Original instant coffee powder (NESCAFE Original 1+2) was purchased from Nestle Ltd. (Dongguan, Guangdong, China). Ingredients such as sugar, coffee creamer (glucose syrup), hydrogenated vegetable oil, stabilizer 340ii, 331iii, 452i, casein (contain milk protein), emulsifier (471, 472e), flavoring, anticaking 551, soluble coffee and Sephadex gel G-25 were purchased from GE Healthcare (Fairfield, San Diego, USA). Quinine sulfate, NaCl and NaOH were purchased from Aladdin Reagent Inc. of China. CHO cell line was a gift kindly provided by the Institute of Biochemistry and Cell Biology, Shanghai Institute for Biological Sciences, Chinese Academy of Sciences. RPMI-1640 medium was purchased from HyClone Company Ltd. (USA). Human hepatocellular carcinoma cell line SMMC-7721 was purchased from the Cell Bank of Type Culture Collection of the Chinese Academy of Sciences (Shanghai, China).

2.2. Instrumentation

Transmission electron microscopy (TEM) measurements were performed on a JEOL model JEM-2000EX transmission electron microscope for characterization of the shape and size of the C-dots by depositing them on 400-mesh C-coated Cu grids. Absorption spectra were recorded at room temperature on a UV-2550 UV–vis spectrophometer (Shimadzu, Japan). The steady-state fluorescence and time-resolved fluorescence decays were recorded using a Horiba Jobin Yvon FluoroMax-4 spectrofluorometer and using a 376 nm laser as an excitation source. Time-resolved fluorescence decays were recorded using the time-correlated single photon counting (TCSPC) method. Data analysis was conducted via a commercial software provided by Horiba Instruments. The down conversion and upconversion fluorescence spectra were measured by a PerkinElmer LS55 fluorescence spectrometer. X-ray diffraction (XRD) measurements were carried out using a P analytical XRD instrument in conjunction with Cu Kα radiation (λ=0.15418 nm). X-ray photoelectron spectroscopy (XPS) spectra were used to characterize the chemical composition using an Escalab 250 Xi X-ray photoelectron spectrometer (Thermo Scientific). The Fourier transform infrared spectroscopy (FTIR) spectra were measured by VECTOR 22 with the KBr pellet technique ranging from 500 to 4000 cm^{-1}. The fluorescent microscope images were obtained by using an inverted Olympus IX73 fluorescent microscope with a barrier filter 420 nm for an excitation wavelength between 330 nm and 385 nm, 505 nm for the excitation wavelength between 450 nm and 480 nm, 590 nm for the excitation wavelength between 510 nm and 550 nm.

2.3. C-dots preparation

In a typical preparation process, 4 g of Nescafe® Original instant coffee powder was added into 20 mL of distilled water at 90 °C and the mixture was vigorously stirred and centrifuged at 14,000 rpm for 15 min. The resulting supernatant was further filtered through a 0.22 μm membrane to remove large or agglomerated particles and purified by Sephadex G-25 gel filtration chromatography with pure water as eluent. The fluorescent fractions were collected and other soluble fractions were retained in the column and eluted after the C-dot fractions. The obtained C-dot fractions (~200 mL) were lyophilized and stored at 4 °C for further characterization and use.

2.4. Fluorescence quantum yield (Φ) measurement

Fluorescence quantum yield (Φ) of the C-dots was calculated by using a report method with the following equation[17]:

$$\Phi_1 = \Phi_2 I_1 A_2 \eta_1^2 / I_2 A_1 \eta_2^2 \quad (1)$$

in this equation, I_1 and I_2 are the fluorescence intensities of the C-dots and the standard, and A_1 and A_2 are the optical densities of the C-dots and the standard, respectively. η_1 and η_2 are the refractive indices of the C-dots and the standard, respectively. The standard quantum yield of Φ_2 was 0.54 for quinine sulfate at 360 nm in 0.1 M H_2SO_4 (refractive index: 1.2) and the C-dots were dissolved in water (refractive index: 1.2). To minimize reabsorption effects, absorbance values of the individual solutions in cuvettes were maintained under 0.1 at the excitation wavelength. Excitation and emission slit widths were 4.5 nm for fluorescence spectra measurement.

2.5. Fluorescence lifetime (τ) measurement

Fluorescence lifetime (τ) of the C-dots was calculated using the following equation [18]:

$$\tau = (A_1\tau_1 + A_2\tau_2 + A_3\tau_3)/(A_1 + A_2 + A_3) \quad (2)$$

The average fluorescence lifetime of C-dots is 4.64 ns, wherein A_i is the fractional contributions of time-resolved decay lifetime of τ_i.

τ_i (ns)	A_i (%)
3.20	51.32
0.34	25.58
12.60	23.10

2.6. pH effect on fluorescence intensity of the C-dots

Britton–Robinson buffer consisting of 0.04 mol/L H_3BO_3, 0.04 mol/L H_3PO_4, 0.04 mol/L CH_3COOH was used in the range of pH 2–12. Various pH (pH 2–11) solutions were prepared by adding different amount of 0.2 mol/L of NaOH solution. 2 ml of Britton–Robinson buffer solution was added to 200 μL of C-dots solution (1 mg/mL) and the PL intensity was recorded with the PerkinElmer LS55 fluorescence spectrometer using a 300 nm excitation wavelength and 1200 nm/min scan rate. All the values are the average of triplicate measurements.

2.7. Cytotoxicity assay

In vitro cytocompatibility of the C-dots with CHO cells was investigated. CHO cells (5×10^3 cells/well) were seeded in a 96-well plates in a growth medium consisting of RPMI-1640 medium supplemented with 10% fetal bovine serum and 1% antibiotic–antimycotic solution, and maintained at 37 °C in a humidified 5% CO_2 atmosphere. The cells were treated with various concentrations (0–20 mg/mL) of C-dots and were cultured for another 24 h. At the end of time point, a Cell Counting Kit-8

(CCK-8) (Donjindo Molecular Technologies, Gaithersburg, MD) was used to evaluate the cytotoxicity of the C-dots after incubated in the medium for an additional 3 h. The optical density of each well was measured on a Wellscan Mk3 microplate reader (Labsystems Dragon Ltd., Finland), using a test wavelength of 450 nm and a reference wavelength of 630 nm. Cell viability was calculated as follows:

$$\text{Cell viability}\ (\%) = (A_{\text{sample}} - A_{\text{blank}}) \times 100\%/(A_{\text{control}} - A_{\text{blank}}) \quad (3)$$

where A_{sample} is absorbance of a well with cells, CCK-8 solution and C-dots solution; A_{blank} is absorbance of a well with medium and CCK-8 solution, without cells; A_{control} is absorbance of a well with cells and CCK-8 solution, without C-dots solution. The data was expressed as the percentages of viable cells compared to the survival of a control group (untreated cells as controls of 100% viability).

2.8. In vitro cell imaging

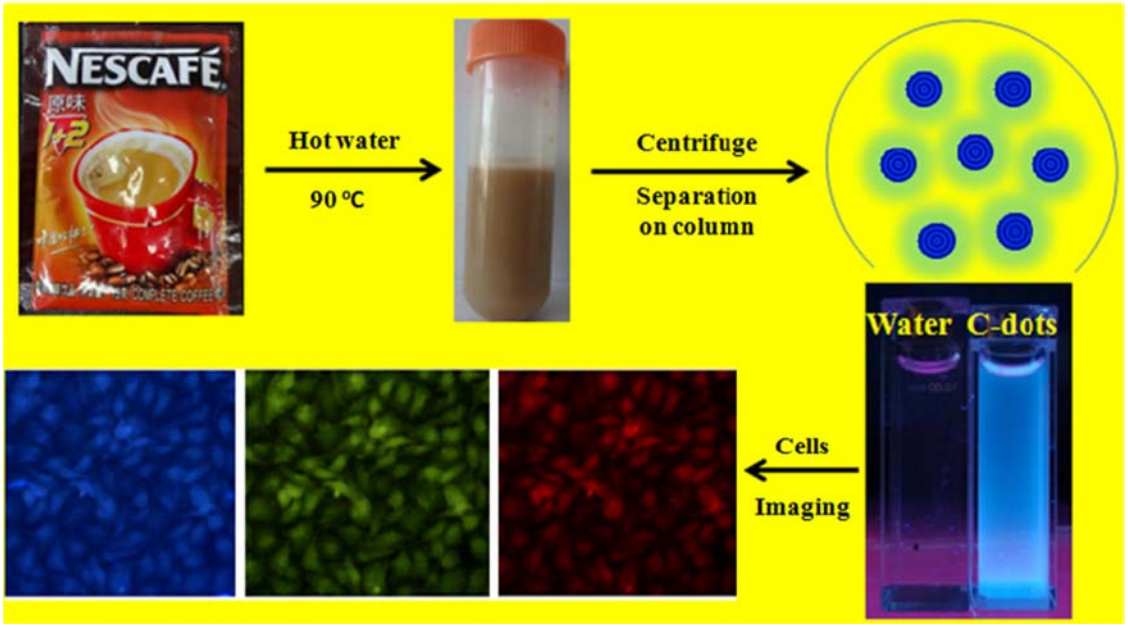
Human hepatocellular carcinoma cell line SMMC-7721cells were maintained in a RPMI-1640 medium with 10% FBS, antibiotic–antimycotic solution L-glutamine (2 mM), and non-essential amino acids (1%) in 5% CO_2 at 37 °C. The cells were trypsinized and seeded in tissue culture plates at an initial cell density of 1×10^5 cells/well. The cells were treated with C-dots at a final concentration of 1.5 mg/mL. After incubated at 37 °C for 24 h, the cells were washed three times with fresh media and imaged with an inverted Olympus IX73 fluorescent microscope with excitation wavelength of 330–385 nm, 450–480 nm and 510–550 nm for blue, green and red region images collection, respectively.

2.9. In vivo small animal imaging

In vivo imaging was carried out with a CRi Meastro Ex *in vivo* imaging system (Caliper Life Sciences Inc., USA). 10 mg of fish food mixed C-dots (1:1, wt/wt) was added to the fish tank where the adult guppy fish inhabited. The fish food without C-dots was added to the control fish tank as a control. After 56 h, the guppy fish was thoroughly rinsed with distilled water and submitted for *in vivo* imaging with a CRi Meastro Ex *in vivo* imaging system. Spectral fluorescence images were obtained using the appropriate filters for C-dots (excitation: 455 nm; emission: 515 nm long-pass filter; acquisition settings: 500–750 nm in 10 nm steps). Exposure times were automatically calculated and the acquisition setting was recorded as 1500 ms.

3. Results and discussion

Instant coffee, also known as soluble coffee or coffee powder, is a beverage prepared from brewed coffee beans which is commercially



Scheme 1. Photoluminescent C-dots prepared from Nescafe® Original instant coffee.

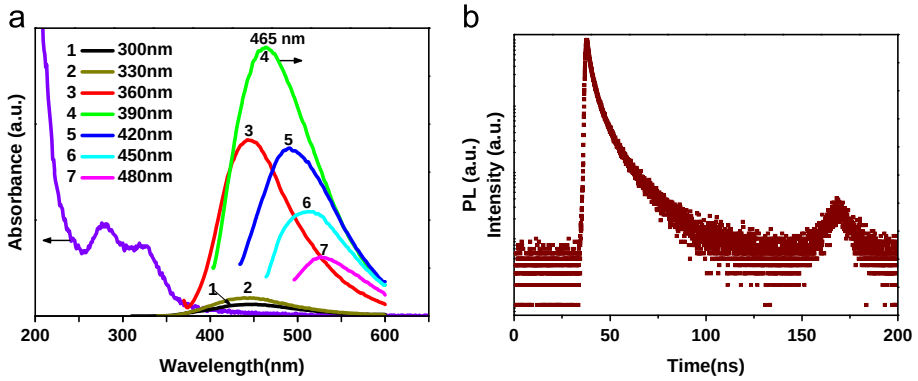


Fig. 1. UV–vis absorption and PL emission spectra (a) and PL decay curve (b) of C-dots extracted from Nescafe® Original instant coffee.

produced by either freeze-drying or spray drying. Advantages of instant coffee include speed of solubility in hot water, shipping weight and volume lower than beans or ground coffee (to prepare the same amount of beverage), and long shelf life. [18] Nescafé, Extra, Folgers, Maxwell House and Starbucks VIA are all popular instant coffee brands in the current market. In this study, we chose commercial Nescafe® Original instant coffee as a raw material to prepare C-dots because of the photoluminescence observed in Nescafe Original instant coffee. Briefly, the C-dots were isolated from commercial Nescafe® Original instant coffee as illustrated in Scheme 1. The isolation process of the C-dots was quite simple and required centrifugation and column chromatographic separation only after treating the coffee sample with hot water at 90 °C. The overall production yield of the C-dots is about 2% as calculated from the instant coffee powder. Interestingly, the C-dots still can be smelt with the fragrance of the instant coffee. The formation the photoluminescent C-dots in Nescafe® Original instant coffee possibly involves the roasting process, which is used to bring out flavor and aroma during the production of the instant coffee [18].

The obtained C-dots were analyzed by UV–vis and fluorescence spectroscopy. As shown in Fig. 1a, the UV–vis spectrum of the extracted C-dots consisted of two peaks between 250 nm and 360 nm. In addition, a strong background upto 450 nm was observed. The peaks and the background extinction were similar to that of previously reported C-dots. [19] Note that strong PL emission of the C-dots was found when they were excited with UV–vis light between 300 nm and 480 nm, indicating the presence of the C-dots in coffee. The inset in Scheme 1 shows the optical photograph of C-dots aqueous solution irradiated by a 365 nm UV lamp and the PL was strong enough to be seen with the naked eye. The C-dots exhibited an excitation-dependent emission behavior, *viz*. with the increase of excitation wavelength, the C-dots emitting at longer wavelength. The emission intensity shows the highest valve of 465 nm under the excitation at 390 nm. The bathochromic emission of the C-dots is consistent with the previous reports [8,13,17,19]. This overall complex behavior of the PL emission spectra is apparently associated with a variety of emission centers present in the C-dots suspensions [9]. To confirm this, we measured the decay of PL emission and found that it was non-monoexponential for the C-dots suspension with an average life-time of 4.64 ns (Fig. 1b). The proposed PL mechanism is possibly due to the radiative recombination of the energy-trapping sites in the C-dots [5]. The QY of the extracted C-dots at 390 nm was measured to be 5.5%, by calibrating against quinine sulfate, which was much higher than that of the C-dots found in carbohydrate based food caramels [16]. The strongly photoluminescent C-dots will be beneficial to their applications in bioimaging.

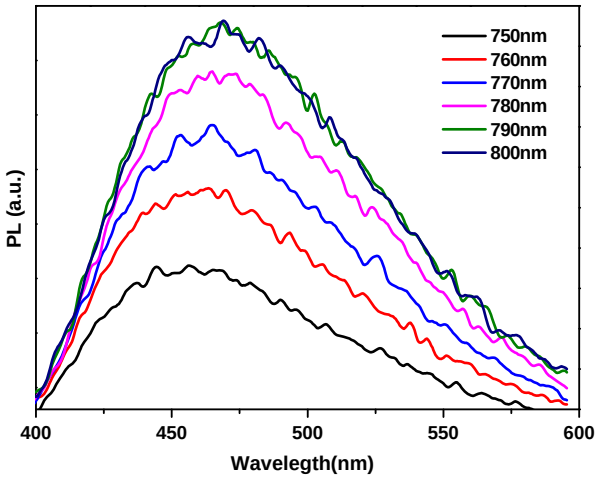


Fig. 2. Upconversion PL emission spectra of C-dots extracted from the Nescafe® Original instant coffee excited in the NIR region.

Significantly, the extracted C-dots were found to possess clear upconversion PL properties as shown in Fig. 2. Upon excitation in the NIR region, the PL spectra show varying emission peaks between 460 nm and 475 nm, which are different from the previous reports that the emission peaks at the same wavelengths as the excitation wavelength varies [20]. Since the energy difference between the excitation and emission in the upconversion process is not a fixed value, the upconversion mechanism of C-dots is more possibly attributed to the multiphoton active process due to the simultaneous absorption of two or more photons leading to the emission of light at a shorter wavelength than the excitation wavelength (anti-Stokes type emission) [20]. The upconversion property of the C-dots is expected to be useful for cell imaging with two-photon luminescence microscopy applications.

Transmission electron microscopy (TEM) image of the C-dots shows that they are roughly spherical particles with the diameter around 4.4 nm (Fig. 3a). The TEM result revealed that the C-dots were present in the Nescafe® Original instant coffee. The size distribution of the C-dots was relatively small with the majority falling within 3–6 nm based on the statistical analysis of 100 particles (Fig. 3b). XRD analysis of the powder C-dots (Fig. 4a) shows a broad peak at about $2\theta = 21^\circ$ and no sign for its crystalline nature could be found, indicating that the C-dots in the Nescafe® Original instant coffee possibly consist of amorphous carbon, which is well consistent with the result of carbon nanoparticles

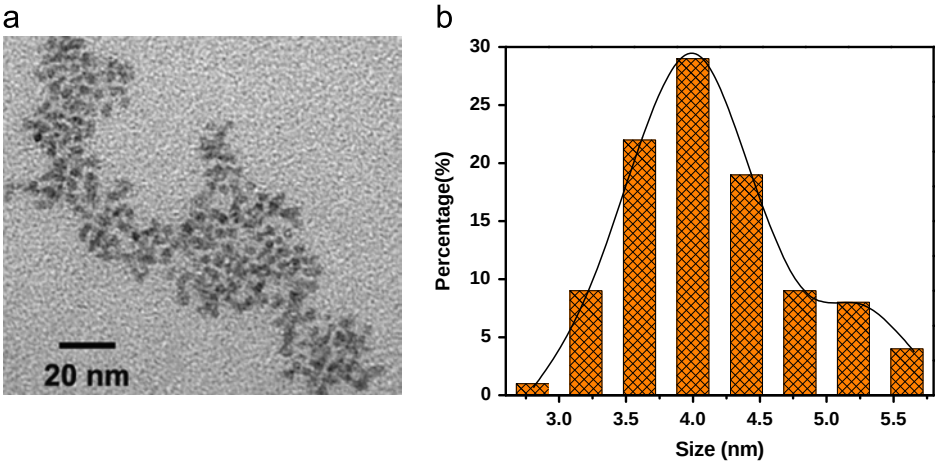


Fig. 3. TEM image (a) and size distribution histogram (b) of C-dots from the Nescafe® Original instant coffee.

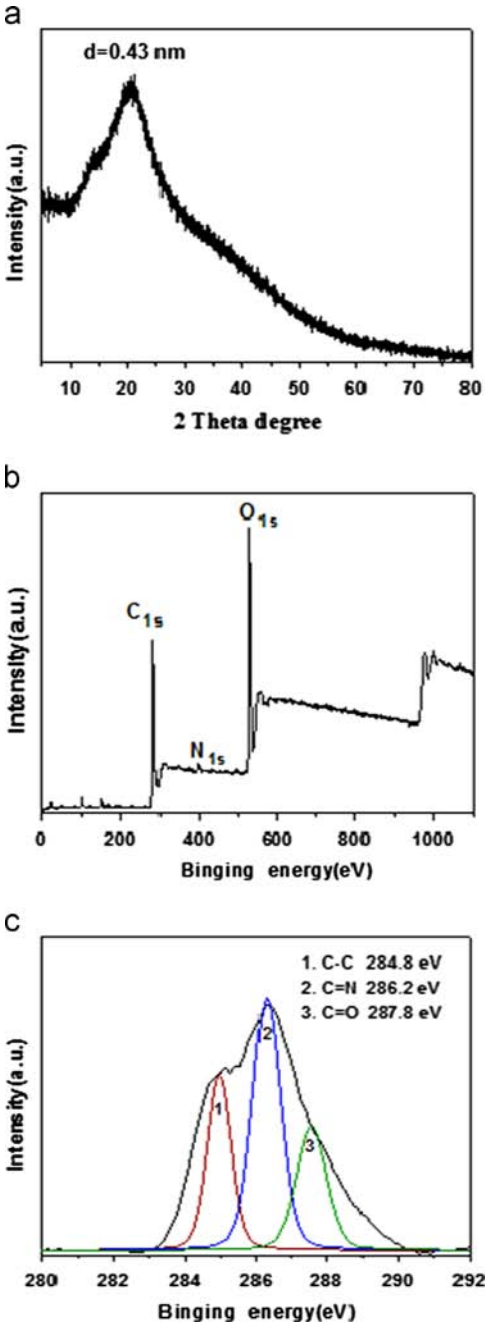


Fig. 4. Powder X-ray diffraction (XRD) pattern: (a) X-ray photoelectron spectroscopy (XPS) spectrum (b) and high-resolution XPS spectra of C 1s (c) of C-dots extracted from the Nescafe® Original instant coffee.

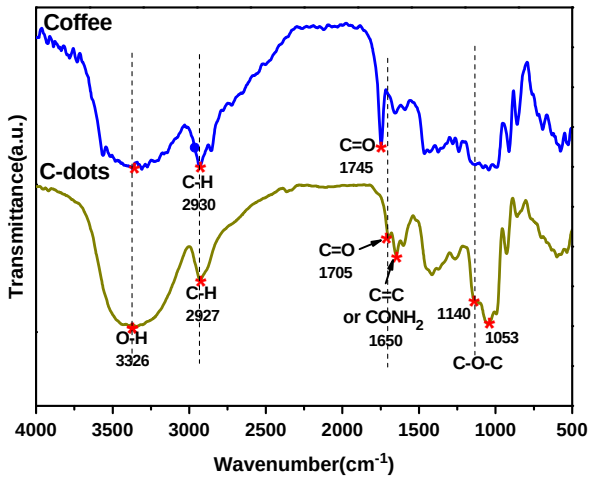


Fig. 5. FT-IR spectra of coffee powder and C-dots extracted from the Nescafe® Original instant coffee.

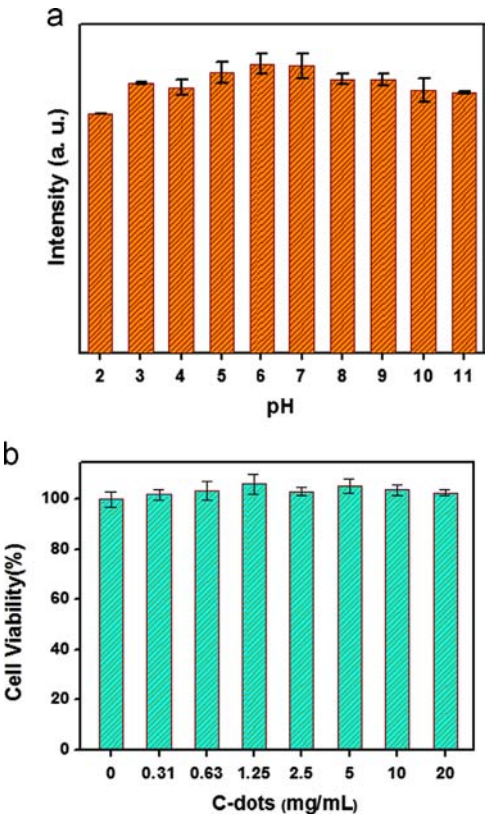


Fig. 6. pH effect on the PL intensity at 465 nm (λ_{ex}=390 nm) (a) and cytotoxicity (b) of C-dots extracted from the Nescafe® Original instant coffee. All the values are the average of triplicate measurements.

extracted from the caramels of bread, jaggery, sugar caramel, corn flakes and biscuits [16]. The elements analysis of XPS showed two predominant peaks at 285 eV, 532 eV and a weaker peak at 399.4 eV (Fig. 4b), which were associated with three elements namely C, O and N, respectively. Their relative contents were *ca.* 30.1%, 62.2% and 7.8% on the basis ofcalculations of the integral area. The results illustrated that the C-dots are actually a kind of N-doped C-dots. The predominant O peak may generate from H_2O, O_2 or CO_2 molecules absorbed on the surface of the C-dots, which is similar to that of C-dots derived from CCl_4 and $NaNH_2$ [21]. High-resolution XPS spectra of C 1s in Fig. 4c could be fitted into three peaks at 284.8, 286.2 and 287.8 eV, which were attributed to C–C, C=N and C=O bonds, respectively. [20] The results clearly indicated that the C-dots contained C, O and N elements in the Nescafe® Original instant coffee which may be functionalized with hydroxyl and carboxylic acid groups.

FTIR spectra analysis was also performed to gain further structural insights into C-dots. As depicted in Fig. 5, a broad and intense peak around 3326 cm^{-1} for both coffee powder and C-dots was attributed to the O–H stretching vibration, indicating the existence of large numbers of hydroxyl groups. The peak at 2927 cm^{-1} corresponds to the C–H vibrations of methylene. Unlike the coffee powder, the C-dots show the predominant peaks of C=O group at 1705 cm^{-1} and C=C double bonds or $CONH_2$ amide carbonyl at 1650 cm^{-1}. Other strong peaks with increased

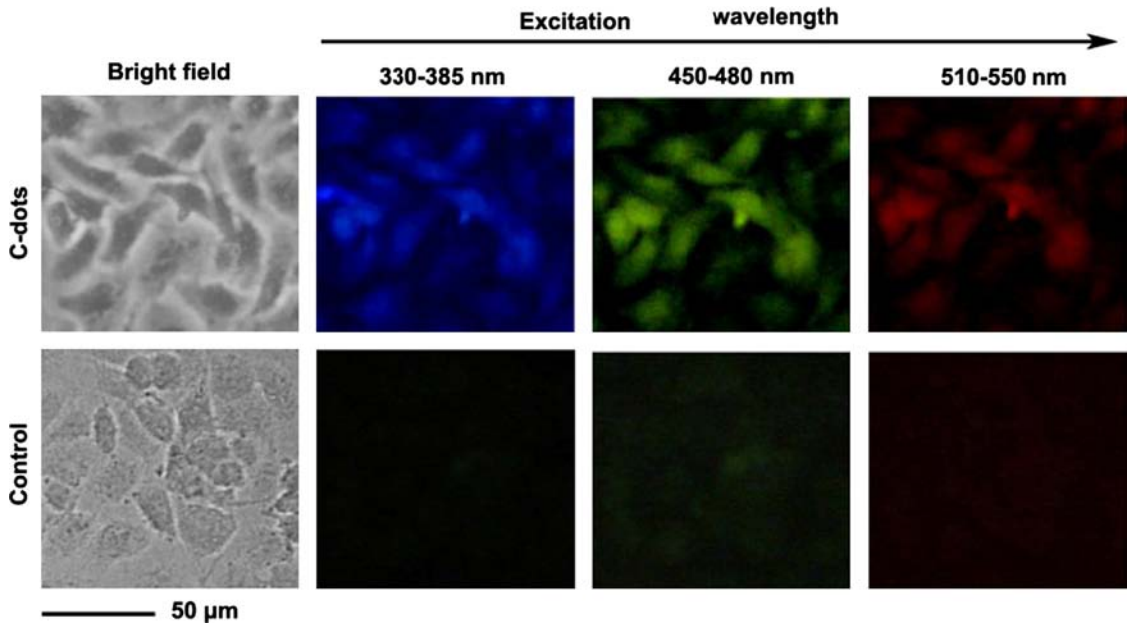


Fig. 7. Bright field and fluorescence microscope images of human hepatocellular carcinoma cells incubated with C-dots from the Nescafe® Original instant coffee for 24 h. Exposure time was 400 ms.

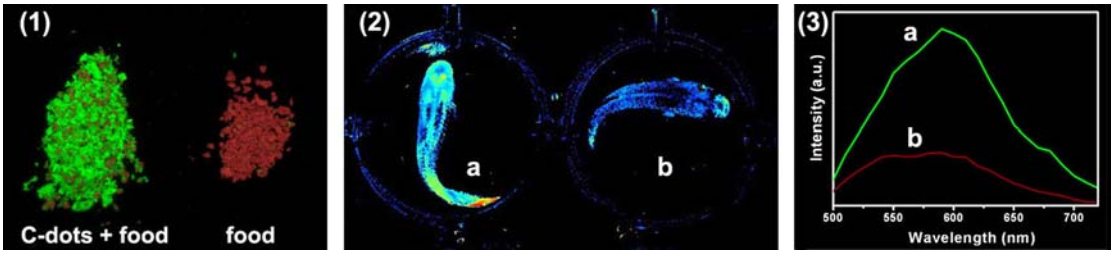


Fig. 8. Unmixed fluorescence images of fish food (1) and fish treated with C-dot-food mixture (2a) and its control (2b). PL spectra of the fish treated with C-dot-food mixture (3a) and its control (3b). Excitation: 455 nm; emission: 490 nm, long-pass filter, acquisition settings: 500–750 nm in 10 nm steps. Exposure time was automatically calculated and the acquisition setting was 1500 ms.

intensity at 1140 and 1053 cm^{-1} indicated the existence of aromatic alkoxy bonds of the C-dots. Notably, majority of the groups on the particle surface contain the oxygen element, which is well consistent with the XPS analysis result of high oxygen content of the C-dots. Thus the above results demonstrated that the C-dots from the Nescafe® Original instant coffee consist of various surface groups such as –OH and –COOH for potential biological applications in conjugating drug or targeting moieties.

In addition, we also investigated the pH value of the C-dots aqueous solution effect on the PL intensity of the C-dots. Unlike the C-dots prepared from candle soot [22], the PL intensity of the C-dots showed a pH independent behavior by varying the pH value from 2 to 11 (Fig. 6a), which was consistent with the results reported by Wang et al [12]. This demonstrated that the radiative recombination of the energy-trapping sites on the C-dots was not significantly affected by varying the pH value from alkaline to acidic, indicating that the C-dots might have potential biological applications in a wide pH range. Moreover, instant coffee has been consumed for more than 120 years by people around the world and the Nescafé brand was launched into the market more than 70 years ago [18]. They are hardly considered as a toxic drink and the C-dots extracted from instant coffee may have good biocompatibility for their applications in bio-medical fields. To prove this point, the cytotoxicity of C-dots was evaluated after the CHO cells were treated with different doses of C-dots by a CCK-8 assay. As shown in Fig. 6b, no visible reduction of cell viability was found with a concentration as high as 20 mg/mL for up to 24 h exposure time. Thus the C-dots derived from instant coffee might be considered safe at a concentration less than 20 mg/mL. However, a huge volume of experiments are required to further study their safety issue for the new carbon nanomaterials in future biomedical applications.

To assess the potential application of the C-dots derived from the Nescafe® Original instant coffee as fluorescent probes, *in vitro* cellular uptake experiment of the C-dots was performed in human hepatocellular carcinoma cells. Fig. 7 shows the bright field and fluorescent microscope images excited at different wavelengths. The hepatocellular carcinoma cells incubated with C-dots become bright as compared with the control cells without adding the C-dots. The excitation dependent PL of the extracted C-dots made it possible for multiple color emission in cells imaged by using C-dots only. The results indicated that the C-dots were able to be used for *in vitro* carcinoma cells labeling via a simple incubation method. We also investigated the possibility of the C-dots from coffee for small animal fluorescent imaging by feeding guppy fish with C-dots mixed food. The guppy fish were selected because they are small aquatic craniate animals, in which the fluorescence signal can be easily observed with a Meastro *in vivo* imaging system. As shown in Fig. 8, strong PL of the C-dot-food mixture was observed as compared with the control (fish food), indicating that the PL was coming from C-dots rather than fish food. The guppy fish fed with C-dot-food mixture clearly showed the

enhanced PL with a signal-to-noise (S/N) ratio of 2.27 (Fig. 8(2a)), which was much higher than that of the control fish (Fig. 8(2b)). Fluorescence spectra analysis result demonstrated that the PL signal (Fig. 8(3a)) was coming from the coffee C-dots. The tested fish was alive within the period of observation up to four weeks, revealing that C-dots with low biotoxicity might have potential for *in vivo* small animal imaging.

4. Conclusions

In summary, our current work demonstrated the presence of the C-dots in the Nescafe® Original instant coffee. The strongly photoluminescent C-dots exhibited an excitation-dependent emission behavior, interesting upconversion photoluminescent property and excellent pH stability in a wide pH range. The coffee derived C-dots did not impose any significant toxicity to cells and could be directly applied in the imaging of carcinoma cells and small guppy fish without further functionalization. Our finding of the presence of C-dots in human drinks may help their potential applications in cell tracking and more practical biological applications.

Acknowledgments

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