Preparation of Biomass-Based Carbon Dots with Aggregation Luminescence Enhancement from Hydrogenated Rosin for Biological Imaging and Detection of Fe$^{3+}$

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ABSTRACT: Fluorescent carbon dots (CDs) have numerous important applications, but enhancing the fluorescence emission and overcoming fluorescence quenching are still big challenges. Here, fluorescence-enhanced carbon dots (named hr-CDs) were prepared from sustainable hydrogenated rosin, using a simple hydrothermal method in a water solvent. The hr-CDs were mainly composed of graphitized carbon cores with surface functional groups. With the increase in the concentration to hr-CDs aqueous solutions, the distance between the carbon cores decreased, which resulted in the formation of J aggregates and the enhanced blue fluorescence emission. Even in the solid state, the hr-CDs show fluorescence emission because the surface functional groups could prevent π−π stacking interactions between the carbon cores. The hr-CDs show excellent resistance to photobleaching under intense ultraviolet light (200 mW/cm²). Vibrations and rotations of graphitized carbon core are restricted by low temperature and high viscosity, leading to increased radiative transition and thus increase in fluorescence intensity. The pH value in the range of 3.99−9.87 and anions have little effect on the fluorescence emission of hr-CDs. The fluorescence emission of the hr-CDs was selectively quenched by Fe$^{3+}$ and can thus be used to detect Fe$^{3+}$. The hr-CDs also have good biocompatibility and show the same ability in cell nuclear staining as 4′,6-diamidino-2-phenylindole (DAPI).

INTRODUCTION

There have recently been numerous peer-reviewed articles that describe carbon dots (CDs) with excellent optical properties and discuss their potential as substitutes for conventional fluorescent materials, such as fluorescent organic dyes and inorganic fluorescent nanoparticles.1−4 Because of their many advantages, including tunable fluorescence, low toxicity, good biocompatibility, and resistance to photobleaching,5−11 CDs have been widely used as biomarkers, photocatalysts, and white light emitting diodes (WLEDs).8,12−16 Many kinds of raw materials, which can be broadly classified as either organic materials derived from industrial synthesis17,18 or naturally occurring biomass materials,19 have been successfully converted into CDs using increasingly sophisticated synthetic methods.20,21 Simple and economical methods for converting low-cost renewable biomass materials into CDs, especially, have received much attention recently. A wide variety of renewable biomass materials, including corn,21 starch,22 enokitake mushrooms,23 various fruits,24−26 rice husks,27,28 chitosan,29 alkali lignin,30 and willow catkins31 have now been used to prepare CDs. Taking every factor into account, however, current methods for producing CDs all have shortcomings. In many regions of the world, food is in short supply and it is wasteful to use edible materials to prepare CDs. Reported technologies to synthesize CDs also usually require high-temperature calcination, strong acid or strong alkali for deep carbonization,32 or extraction with organic solvents,33 which require massive consumption of energy and materials. Another drawback is that the fluorescence of many CDs is quenched in more concentrated solutions. Some CDs totally lose their fluorescence in the solid state by a process known as aggregation-caused quenching (ACQ), which is caused by fluorescence resonance energy transfer and direct π−π interactions.34 ACQ remains the Achilles heel that restricts the wider application of CDs. Some CDs, however, show aggregation-induced emission enhancement (AIEE) instead and avoid fluorescence attenuation by radiative recombination.35,36 There is currently a real need for novel CDs with...
AIEE. Here, we report a new type of CDs, named hr-CDs, which can be prepared from hydrogenated rosin, a biomass raw material with a unique ternary ring structure, by a one-step hydrothermal method in an aqueous solvent environment, without the need for a dopant or purification, and also avoid the introduction of toxic reagents through a method that is different from the one reported. The preparation of hr-CDs is shown in Scheme 1. The prepared hr-CDs solution emits a blue fluorescence with an enhanced intensity as the concentration is increased. Even in the solid state, the hr-CDs, which have a yellow-green emission, are different from the conventional carbon dots with aggregation fluorescence quenching in the solid state. The hr-CDs can be used not only as a fluorescent probe for detecting Fe3+ but also for cell imaging.

**RESULTS AND DISCUSSION**

**Characterization of hr-CDs.** The as-prepared hr-CDs were dissolved in deionized water and their morphology was investigated by transmission electron microscopy (TEM). The carbon dots possessed a spherical appearance (Figure 1a), with an average diameter of 1.5 nm (Figure S1). The lattice fringes of the hr-CDs display interplanar spacings of 0.21 and 0.24 nm (Figure 1a, inset), which correspond to the (100) plane of graphitic carbon and the (1120) lattice fringes of graphene, respectively. In the UV−vis spectra (Figure 1b), compared with hydrogenated rosin, the hr-CDs showed significantly enhanced absorption over the range 247−320 nm due to the absorption bands of π−π* and n−π* transitions. Since the spectra of hydrogenated rosin and hr-CDs were determined at the same concentration, this indicates a more conjugated structure in the hr-CDs, compared with hydrogenated rosin. X-ray diffraction analysis showed that the diffraction peak position of the graphite carbon cores is noticeably influenced by the structure of the raw material (Figure S2). The Fourier transform infrared (FTIR) spectrum of the hr-CDs (Figure 1c) showed that peaks were consistent with hydrogenated rosin. Proton nuclear magnetic resonance (1H NMR) spectra (Figure 1d) were used to determine the structure of the hr-CDs. Aromatic H signals seen in the range of 6.0−8.0 ppm may be attributable to graphitized carbon core proton resonance. Analysis of the hr-CDs by high-resolution X-ray photoelectron spectroscopy (XPS) of C 1s (Figure 1e) and O 1s (Figure 1f) indicated the presence of C−C/C=C−C, C=O, C−O, and O−C=O groups. The above results proved the existence of the basic structural−functional group unit molecule of hydrogenated rosin on the surface of the core carbon.
Figure 2. (a) Fluorescence spectra of an aqueous solution of hr-CDs (20 μg/mL) at different excitation wavelengths (inset: photograph showing the fluorescence of aqueous solution of hr-CDs under 365 nm ultraviolet irradiation). (b) Fluorescence spectra of the aqueous solutions of hr-CDs with different concentrations (Ex = 310 nm). (c) Fluorescence spectra of solid hr-CDs (inset: photograph showing fluorescence of solid hr-CDs under 365 nm ultraviolet irradiation). (d) Fluorescence intensity of aqueous solution of hr-CDs (10 μg/mL) and DAPI (10 μg/mL) after irradiation with UV lamp (200 mW/cm²) for different periods of time.

decreased by ~25% in the first 60 min and then remained stable (Figures 2d and S4). The fluorescence intensity of DAPI, on the other hand, continued to decrease after 60 min, with a total reduction of ~80% after 180 min (Figure 2d). It is worth noting that the UV irradiance that we use is 200 mW/cm², which is 2000-fold higher than the intensity used in a recently reported study. 45

The fluorescent intensity of carbon dots is influenced by factors such as pH, temperature, metal ions, and some anions. To better understand the potential applications of hr-CDs, we next investigated the effect of pH on fluorescence intensity. The fluorescence intensity of the hr-CDs was stable, with little obvious changes, over the pH range of 3.99–9.87 (Figures 3a and S5). This is the pH range of intracellular microenvironments, 28 suggesting that the hr-CDs are suitable for cellular imaging. The fluorescence intensity of an aqueous solution of hr-CDs decreased as the temperature increased (Figures 3b and S6). Since vibration and rotation of graphitized carbon core with functional groups are restricted at lower temperatures, there is increased radiative transition and thus increased fluorescence intensity. 45 The effect of viscosity on the fluorescence intensity of hr-CDs was investigated using different proportions of water and glycerin as the solvent. The fluorescence intensity increased with increasing amounts of glycerin (Figures 3c and S7) because the higher viscosity inhibits the vibration and rotation of the carbon dots, thus increasing the radiative transitions.

Selectivity and Sensitivity of hr-CDs. The experiment was carried out to test the fluorescent response of the hr-CDs to various anions (Figures 3d and S8) and cations (Figures 3e and S9) by adding the test ion (50 μM) to an aqueous solution of hr-CDs (20 μg/mL). F₀ is the fluorescence intensity of the solution of hr-CDs without added ions and F is the intensity of the solution with added ions. A wide variety of anions had very little effect on the fluorescence intensity (Figures 3d and S8).

Cations, on the other hand, had different individual effects on the fluorescence intensity (Figures 3e and S9). The most obvious quenching was caused by Fe³⁺ (Figure 3e), likely because the open d orbitals of Fe³⁺ can coordinate easily with the hydroxyl groups. 28 When Fe³⁺ binds to the hr-CDs, which act as electron donors, the d orbitals of the Fe³⁺ split. Some electrons in the excited state are then transferred from the hr-CDs to the d orbitals of Fe³⁺, reducing the proportion of radiative transition and leading to fluorescence quenching. 45

Then, we explored the feasibility of using hr-CDs for the detection of Fe³⁺ (Figure S10). On the addition of Fe³⁺, there was a marked decrease in fluorescence intensity, and in the range of 0–60 μM, the Fe³⁺ concentration fits well with the fluorescence intensity ratio (F₀/F) by linear equation (Figure 3f) and the equation is F₀/F = 0.00845C + 0.9781, where the C is the concentration of Fe³⁺. The detection limit was about 6.16 μM, which was lower than that reported by the previous Fe³⁺ detection systems based on CDs. 47,48

Cytotoxicity and Cell Imaging of hr-CDs. For years, CDs have been reported to achieve outstanding imaging quality in cell biology. To demonstrate the potential of hr-CDs to replace the previously described CDs, we investigated the inherent cytotoxicity and biocompatibility of hr-CDs in MG-63 and human umbilical vein endothelial cells (HUVECs) using standard cell counting kit-8 (CCK-8) assays. The hr-CDs showed excellent biocompatibility with MG-63 (Figure 4a).
and HUVECs (Figure 4b). Flow cytometry was used to assess cell apoptosis in MG-63 and HUVECs treated with hr-CDs (50 μg/mL) for 72 h. The percentages of apoptotic (Q2 + Q4) MG-63 cells and HUVECs were 10% (Figure 4c) and 7.8% (Figure 4d), respectively, which are no higher than that for normal cell apoptosis (10%).

The hr-CDs were next investigated as a biological dye and incubated with MG-63 and HUVECs for 10 h in a bioimaging study. Images of MG-63 and HUVECs stained with DAPI, which produces a blue color under UV light, are shown in Figure 5a-I,b-I. The images showing a green color under blue light (Figure 5a-II,b-II) are those stained with hr-CDs. DAPI is commonly used as a cell nuclear stain and the images stained by DAPI and hr-CDs overlapped well (Figure 5a-III,b-III), demonstrating that the hr-CDs are also an effective cell nuclear stain.

## CONCLUSIONS

Hydrogenated rosin was used as the raw material to synthesize hr-CDs using a simple hydrothermal method. Upon irradiation with 365 nm light, an aqueous solution of hr-CDs and solid hr-CDs emitted blue and yellow-green fluorescence, respectively. Importantly, the hr-CDs had excellent resistance to photobleaching when irradiated with ultraviolet light (200 mW/cm²), which is 2000-fold higher than the intensity used in a recent report. The hr-CDs could also be used to detect Fe³⁺, with a detection limit of 6.16 μM. Because of their inherent biocompatibility and low cytotoxicity, the hr-CDs could be used as a cell nuclear stain that is as effective as the commonly used cell nuclear stain, DAPI.

## EXPERIMENTAL SECTION

**Materials.** Hydrogenated rosin (acid value, 170.7 mg KOH/g, specific information is recorded in Table S1) was purchased from Guangxi Hualin Chemical Co., Ltd., China, and DAPI was purchased from Shanghai McLean Biochemical Reagents Co., Ltd., China. Al(NO₃)₃·9H₂O, Ca(NO₃)₂·4H₂O, Cd(NO₃)₂·4H₂O, Cu(NO₃)₂·3H₂O, and Fe(NO₃)₃·9H₂O were purchased from Tianjin Bodi Chemical Industry Co., Ltd., China. Ni(NO₃)₂·6H₂O, Pb(NO₃)₂, Sr(NO₃)₂, Zn(NO₃)₂·6H₂O, Ba(NO₃)₂, CH₃COONa, CH₃COONa, glycerol, and NaNO₂ were purchased from Tianjin Fuyu Fine Chemical Co., Ltd., China. EDTA-2Na, B₂O₃·Na₂, C₂O₄·Na₂, Na₂CO₃·Na₂, Na₂PO₄, NaCl, NaF, NaH₂PO₄, and NaHCO₃ were purchased from Tianjin Yongda Chemical Reagent Co., Ltd., China. All reagents were analytical grade and used as received without further purification. Deionized water was prepared using a Clever-Q30 UT water filtration system Zhiang Instrument Co., Ltd. (Shanghai, China). A cell counting kit-8 (CCK-8) assay kit was purchased from Dojindo Laboratories (Kumamoto, Japan), and Normocin was purchased from InvivoGen (San Diego). Fetal bovine serum (FBS), Dulbecco’s modified Eagle’s medium/Ham’s F12 medium (DMEM/F12), and phosphate-buffered saline (PBS) solution were purchased from Gibco and Thermo Fisher Scientific Inc. (Waltham). MG-63 cells and HUVECs

![Figure 4](image_url)

**Figure 4.** (a, b) Relative viability of MG-63 and HUVECs incubated with a series of gradient concentrations of hr-CDs for 24 h. Cytotoxicity was evaluated by flow cytometry using (c) MG-63 cells and (d) HUVECs treated with hr-CDs (50 μg/mL) for 72 h.

![Figure 5](image_url)

**Figure 5.** Fluorescence images of (a) MG-63 cells and (b) HUVECs stained by DAPI and incubated with hr-CDs for 10 h. Imaging stained by DAPI in nucleus (I), imaging stained by hr-CDs in nucleus (II), and overlays of the previous two (III).
were purchased from the Chinese Academy of Sciences (Shanghai, China).

**Characterization.** Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HR-TEM) images were collected using a JEM-2100 transmission electron microscope (JEOL, Ltd., Tokyo, Japan). Proton nuclear magnetic resonance (1H NMR) spectra were measured in dimethyl sulfoxide (DMSO) using an AVANCE III HD 500 MHz spectrometer (BrukerCorp, Karlsruhe, Germany). X-ray photoelectron spectroscopy (XPS) was carried out using an Escalab 250Xi X-ray photoelectron spectrometer (Thermo Fisher Scientific Co., Ltd., Shanghai, China). The FTIR spectra were collected using a frontier Fourier transform infrared spectrometer (PerkinElmer Co., Ltd., Waltham, MA). The UV–vis absorption spectra were recorded using a TU-1950 ultraviolet–visible spectrophotometer (Persee General Instrument Co., Ltd., Beijing, China).

**Synthesis of hr-CDs.** Hydrogenated rosin (0.7 g) was ground to a powder and placed in a 100 mL Teflon-lined stainless autoclave together with deionized water (70 mL). The mixture was heated to 180 °C for 12 h and then allowed to cool to room temperature. The resulting solution was filtered through a 0.22 μm ultrafiltration membrane and then freeze-dried to provide the hr-CDs.

**Cytotoxicity Test.** The effects of different concentrations of hr-CDs on the viability of HUVECs and MG-63 were determined using a cell counting kit-8 (CCK-8) assay. Cell suspensions, harvested at the exponential growth phase of the cells, were plated onto a 96-well plate at a density of 5000 cells/well. The cells were then grown overnight at 37 °C and cultured at 37 °C in a humidified atmosphere of 5% CO2 for 24 h. Cytotoxicity test (CCK-8) was performed using a Multiskan GO microplate reader (Thermo Fisher Scientific, Vantaan, Finland). Cell viability was defined as the ratio of absorbance in the presence of hr-CDs to that in the absence of hr-CDs.

\[
\text{cell viability (％)} = \left( \frac{\text{OD}_{\text{test}} - \text{OD}_{\text{blank control}}} {\text{OD}_{\text{negative control}} - \text{OD}_{\text{blank control}}} \right) \times 100\%
\]

**Cellular Imaging.** HUVECs and MG-63 were inoculated into 48-well plates (10 000 cells/well) with clean cover glass and cultured at 37 °C in a humidified atmosphere of 5% CO2 for 24 h. Culture medium (10% FBS + 90% DMEM/F12 + 100 μg/mL Normocin) was added, and the cells were cultured with hr-CDs in a saturated humidity incubator at 37 °C under an atmosphere of 5% CO2 for 10 h. The cover glass was removed and washed three times with PBS. The cells were immobilized with a precooled 4% paraformaldehyde solution for 30 min and then dyed using a solution of DAPI in PBS (10 μg/mL) for 5 min. After each operation, the cover glass was washed three times with PBS. The cover glass was sealed with anti-fluorescence quenching agent and images were captured using an inverted fluorescence microscope.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c01527.

Size distribution histograms of hr-CDs; XRD of hr-CDs and hydrogenated rosin; FL decay spectrum and fitted curves of hr-CDs solutions; fluorescence spectra of aqueous solutions of hr-CDs (10 μg/mL) after irradiation with a UV lamp (200 mW/cm²) for different periods of time; fluorescence spectra of aqueous solutions of hr-CDs (10 μg/mL) at different pH values; fluorescence spectra of aqueous solutions of hr-CDs (20 μg/mL) at different temperatures; fluorescence spectra of solutions of hr-CDs (20 μg/mL) in different mixtures of water and glycerol; fluorescence spectra of an aqueous solution of hr-CDs (20 μg/mL) on the addition of different anions; fluorescence spectra of an aqueous solution of hr-CDs (20 μg/mL) on the addition of different cations; fluorescence spectra of an aqueous solution of hr-CDs (20 μg/mL) in the presence of different concentrations of Fe³⁺ (PDF)

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Author Contributions
J.Z. and M.G. contributed equally to this work. S.H. conceived the idea and supervised the material synthesis and data collection for the paper. M.G. and J.Z. conducted the synthesis experiments. Z.P. conducted the cytotoxicity and cell imaging experiments. Y.H., J.N., and X.H. prepared the manuscript. S.H. and S.L. discussed the photoluminescence mechanism of hr-CdS. J.Z. wrote the first draft of the manuscript. S.H., Y.L., and S.L. made substantial revisions. All authors read and approved the final manuscript.

Notes
The authors declare no competing financial interest.

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