Fluorescent carbon dots with excellent moisture retention capability for moisturizing lipstick

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Abstract

Long-lasting moisture retention is a huge challenge to humectants, and effective methods or additives for promote these functions are limited, especially nano-additives. Carbon dots (CDs) have attracted increasing research interest due to its ultra-small size, excellent optical properties and low toxicity, etc. However, most of researches have been focused on the photoexcited CDs and its subsequent photophysical and chemical processes, such as photoluminescence, photodynamic, photothermal and photocatalytic behavior. The intrinsic chemo-physical properties of the pristine CDs are not fully explored. Here, we report an excellent moisture retention capability of a new carmine cochineal-derived CDs (Car-CDs) for the first time. The relationship between the structure of Car-CDs and its moisture retention capability is revealed. More interestingly, the effective applications of Car-CDs in moisturizing lipstick are demonstrated. This work expands the research and application of CDs into a broad, new area, potentially in skin care.

Keywords: Carbon dots, Nano-additives, Moisture retention, Moisturizing appreciation rate, Skin care

Introduction

Humectants have been widely used in food, medicine, and cosmetics owing to their excellent water stabilization capacity during storage and transportation of products [1]. Commonly, hydrophilic polyols such as glycerin and propylene glycol are used for moisturizing additives to improve the biocompatibility of the matrix and endow cosmetic products with moisture retention properties. However, long-lasting moisturizing functions is one of the issues for traditional humectants, which makes it difficult to meet industrial demand. Recently, several studies have devoted to the extraction of natural polysaccharides and exploring the potential applications in skin care [2]. Although natural products are renewable, the problems of complicated material preparation and low yield severely limit their practical applications.

Carbon dots (CDs), with excellent tunable optical properties and good biocompatibility, show great promise as sensors, photocatalysis, photoelectric devices, and multifunctional theranostic systems, among others [3–10]. However, extensive studies on CDs have been focused on improving synthetic strategy, surface engineering, and photoluminescence mechanism [11–16]. Thus, deeply explore the intrinsic chemo-physical properties of CDs...
is essential for innovative application in the future. It is well-known that freshly freeze-dried CDs are highly hygroscopic. This ability is closely associated with its surface groups, which consists largely of hydroxyl and carboxyl. Taking into account the excellent water solubility and abundant surface functional groups of CDs, it can be used as a potential humectant. Nevertheless, the research on CDs-based moisturizing systems remains unexplored.

Here, a new type of carmine cochineal-derived CDs (Car-CDs) is synthesized via one-pot solvothermal method. Among commonly-used synthesis methods, the solvothermal synthesis has many advantages such as being economical, easy to handle and with a high efficiency to synthesize CDs from diverse carbon-based precursors. Importantly, we have systematically studied the moisturizing activity of CDs for the first time. In addition, the moisture retention function of Car-CDs in human skin was further evaluated with moisture measurement value method. More interestingly, we use the Car-CDs as a nano-additive in the preparation of moisturizing lipstick, which suggests its potential beneficial application in health or skin care and cosmetics.

Results and discussion
A detailed description of the methods and experiments is included in the Additional file 1. As shown in Fig. 1a, through a solvothermal method from carmine cochineal in N, N-dimethylformamide (DMF) at 160 °C for 6 h [17], the bright pink-emissive CDs (Car-CDs) are synthesized. Figure 1b shows that the transmission electron microscopy (TEM) image of the as-prepared Car-CDs are uniform in shape with an average diameter of 2.9 nm. An average lattice spacing of 0.21 nm, which is corresponding to the (100) facet of graphite [18], can be clearly observed in the high-resolution TEM image of Car-CDs (Additional file 1: Figure S1). In addition, the Raman spectrum of Car-CDs displays two signals at 1359 and 1585 cm$^{-1}$ for D and G bands, respectively (Additional file 1: Figure S2). Commonly, the $I_D/I_G$ ratios are widely used to evaluate the quality of carbon materials [19]. The ratio of $I_D/I_G$ is about 0.63, indicating a high graphitization degree in Car-CDs [20].

The chemical structure and surface functional groups of the Car-CDs were determined by Fourier transform infrared (FT-IR) spectroscopy and X-ray photoelectron...
spectroscopy (XPS). As shown in FT-IR spectrum (Fig. 1c), the two absorption bands at 3285 and 2937 cm\(^{-1}\) can be attributed to the stretching vibrations of \(-\text{OH}\) [21]. Three strong absorption peaks located at 1589, 1436, and 1123 cm\(^{-1}\) correspond to the stretching vibrations of \(\text{C} = \text{O}\), \(\text{C} = \text{C}\) and \(\text{C} - \text{O}\) bonds, respectively [22, 23]. The XPS further confirm the above-mentioned FT-IR results. As shown in Fig. 1d, the Car-CDs mainly consist of C (285.1 eV, at.\% = 74.9) and O (531.4 eV, at.\% = 25.1) elements. In Fig. 1e, the high-resolution C 1 \(s\) spectrum reveals three peaks at 284.5, 285.6, and 288.2 eV assigned to \(\text{C} - \text{C}/\text{C} = \text{C}\), \(\text{C} - \text{O}\), and \(\text{C} = \text{O}\), respectively [24, 25]. The HR XPS O 1 \(s\) spectrum has two peaks, which are attributed to \(\text{C} = \text{O}\) (531.6 eV) and \(\text{C} - \text{O}\) (532.7 eV) bonds, respectively (Fig. 1f) [26].

Subsequently, optical properties of Car-CDs were investigated. Figure 1g shows the absorption and emission spectra of Car-CDs in methanol. The absorption peaks at 213 and 283 nm are ascribed to \(\pi - \pi^*\) and \(n - \pi^*\), respectively [27]. The corresponding photoluminescence (PL) spectrum shows a emission (558 nm) under UV light excitation (283 nm), and their absolute quantum yields (QY) are measured to be 7.87\% (Additional file 1: Figure S3). Contrarily, carmine cochineal exhibit almost no emission in solution under UV irradiation (Additional file 1: Figure S4). Besides, Car-CDs presented significant excitation-independent under different excitation wavelengths [28, 29] (Additional file 1: Figure S5), and the PL lifetime at 558 nm is calculated to be 3.86 ns (Additional file 1: Figure S6).

The moisture retention activities of Car-CDs were further assessed according to the established method [30, 31]. As shown in Fig. 2a, b, Car-CDs exhibit a dose-dependent trend in moisture-absorption ability under different humidity conditions [32]. Moreover, the moisture-absorption ability of Car-CDs at high humidity condition is equivalent to that of glycerin, frequently used as a hygroscopic agent. Similarly, the moisture retention rate of Car-CDs within 48 h at relative humidity of 43\% and 81\% are 78\% and 84\%, respectively (Fig. 2c, d).

To assess the potential applications of as-prepared Car-CDs in biological systems, cytotoxicity and hemocompatibility tests were performed to investigate their biocompatibility in vitro [33]. The MTT results show that
more than 80% HUVEC cells still remain even with the concentration of Car-CDs reaching 300 μg mL$^{-1}$, which agrees well with previous investigations [34] (Fig. 3a). As shown in Fig. 3b, the release of LDH in HUVEC cells exhibit a concentration-dependent effect [35], and the maximum release was less than 300 U L$^{-1}$. Besides, the compatibility of Car-CDs with blood was evaluated by hemolysis assay. It can be seen that Car-CDs causes no significant hemolysis, and the maximum hemolysis rate is 5.2% (Fig. 3c, d). These results indicate that the hemolytic toxicity of Car-CDs to red blood cells (RBCs) is relatively low, which could allow for further blood applications [36].

Inspired by the appreciable moisture retention effect in vitro, the moisturizing performance of Car-CDs on human skin was further evaluated [37]. Ten volunteers were recruited to apply Car-CDs solution to their hands, and the changes in moisture content before and 2 h after the application was compared. It can be observed in Fig. 4a, b that the skin moisture of hands of different volunteers after applying the Car-CDs for 2 h improves to different degrees. Although the moisture content decreased continuously in the volunteers’ hand area, the overall trend is relatively stable, and the improvement rate of moisture is stable in the range of 27–89%. Interestingly, the results show that females have a significantly higher moisturizing appreciation rate (MAR) than males (Fig. 4c). Subsequently, the moisturizing appreciation rates of three other moisturizing products on the market (named X, Y, Z) and glycerol were evaluated. As shown in Fig. 4d, the efficiency of Car-CDs is comparable to that of glycerol and significantly higher than those of several commercially available moisturizing products. Unexpectedly, Car-CDs can also increase the MAR of several other moisturizing products accordingly. As shown in Fig. 4e, the addition of Car-CDs can significantly increase the MAR of X, Y and Z with the maximum increase of 13.94%. Therefore, these results demonstrate Car-CDs as nano-additives of high efficiency that possess moisture retention effects.

Excitingly, we successfully applied Car-CDs to moisturizing lipsticks as shown in Fig. 5a, d. Subsequently, the moisturizing effect of Car-CDs based lipstick on human skin were further evaluated. As shown in Fig. 5b, after volunteer applying Car-CDs-based moisturizing lipstick, the moisture retention on the skin of their

**Fig. 3** a MTT results of HUVEC cells co-incubated with various concentrations of Car-CDs for 24 h. b LDH release from the HUVEC cells treated with Car-CDs at various concentrations. c Hematological evaluation and d photographs of RBCs treated with different dosages of Car-CDs
hands was significantly improved. It can be intuitively observed in Fig. 5c that the MAR of Car-CDs-based lipstick is more excellent. Taking all of the experimental data together, we proposed a possible mechanism for moisture retention capability of Car-CDs. It is well known that hydrophilic groups on the surface of CDs can easily form hydrogen bonds with water molecules, thereby exhibiting moisture absorption properties. For this reason, we evaluated whether the CDs prepared by citric acid (CA-CDs) have a moisturizing effect. As shown in Additional file 1: Figure S7, CA-CDs has no significant moisture retention ability under different humidity conditions, indicating that hydrogen bonding should not be the main reason for the moisture retention performance. According to relevant literature reports [38], CDs possess a crosslink-enhanced (CE) effect, and the ability of their surface functional groups to bind water molecules during the cross-linking process may be further improved. In addition, the surface functional groups of CDs have polymer-like properties [39–41], and can effectively lock water molecules through water absorption and swelling (Fig. 5e) [42]. Since the unique moisturizing properties caused by the combination of CE and polymer swelling effect, CDs has great potential in skin care and cosmetics.

Conclusions
In summary, we have developed a new type of Car-CDs with excellent moisture retention capability. Subsequent human skin tests confirmed that the Car-CDs were as effective as commercial moisturizers. Additionally, Car-CDs can also be used as nano-additives to enhance the moisturizing ability of other moisturizers. Our proposed mechanism is that the special CE effect is combined with the macromolecule swelling effect on the surface of Car-CDs, which are closely bound with the surrounding water. Thereafter, the Car-CDs were successfully used as a nano-additive in the preparation of moisturizing lipstick, which demonstrates its potential application in health or skin care and cosmetics.
Abbreviations
CDs: Carbon dot; Car-CDs: Carmine cochineal-derived CDs; DMF: N,N-Dimethylformamide; TEM: Transmission electron microscopy; FT-IR: Fourier transform infrared; XPS: X-ray photoelectron spectroscopy; PL: Photoluminescence; QY: Quantum yields; LDH: Lactate dehydrogenase; MTT: 3-(4,5-Dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide; RBCs: Red blood cells; MAR: Moisturizing appreciation rate; CE: Crosslink-enhanced.

Supplementary Information
The online version contains supplementary material available at https://doi.org/10.1186/s12951-021-01029-6.

Additional file 1: Fig. S1. High-resolution TEM image of Car-CDs. Fig. S2. Raman spectra of Car-CDs (λ<sub>ex</sub> = 532 nm). Fig. S3. Absolute fluorescence quantum yield of Car-CDs in methanol. Fig. S4. PL emission spectra of the Car-CDs and carmine cochineal under different conditions. Fig. S5. PL emission spectra with different excitation wavelengths of Car-CDs in methanol. Fig. S6. PL lifetime of Car-CDs. Fig. S7. The relationship between hygroscopicity and time at RH = 43% a and RH = 81% b for different samples. The relationship between moisture retention and time at RH = 43% c and RH = 81% d for different samples.

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Authors’ contributions
CD and HB conceived and designed the experiments, and wrote the manuscript; CD, MX and SW performed the experiments; MM and HD collected data; CD and SW analyzed the data; OUA performed editing the manuscript; AW, ZZ, XW and HB coordinated and supervised the work. All authors read and approved the final manuscript.

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Availability of data and materials
All data generated or analyzed during this study are included in this article.

Declarations

Ethics approval and consent to participate
Not applicable for this study.

Consent for publication
We give our consent for the manuscript to be published in Journal of Nanobiotechnology.

Competing interests
The authors declare that they have no competing interests.
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