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Hair-Derived Carbon Dots toward Versatile Multidimensional Fluorescent Materials

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We report a simple and green route for the fabrication of fluorescent carbon dots (CDs), and demonstrate their versatile applications. Hair, a kind of natural and nontoxic raw material, was chosen as the precursor to prepare CDs via a one-step pyrolysis process. The structure and fluorescence properties of the CDs were thoroughly investigated. The obtained CDs can emit bright blue light under UV light with the quantum yield of ca. 17%, and exhibit excitation-, pH- and solvent-dependent fluorescence. The functional groups on the surface of CDs confer these nanomaterials with excellent dispersibility in water and most polar organic solvents, as well as good compatibility with polymer matrices such as poly(methyl methacrylate) and polyvinylpyrrolidone. Then multidimensional CD-polymer hybrid materials, including one-dimensional (1D) microfibers, 2D patterned films and 3D microbeads, were constructed with excellent overall performances, which are useful in fluorescent patterns, flat panel displays and anti-counterfeiting labeling fields.

Introduction

Fluorescent carbon dots (CDs), a new kind of carbon-based nanomaterial, have received increasing attention in recent years owing to their desirable optical properties, chemical inertness, excellent biocompatibility and low toxicity. The superior advantages of fluorescent CDs make them stand out of traditional fluorescent materials (e.g. organic dyes and semiconductor quantum dots), and show promising prospects in candidates for various potential applications, such as bioimaging, sensing, photocatalysts and optoelectronic devices. Up to now, various elegant methods have been developed to fabricate CDs, and they can be generally classified into two main types: top-down and bottom-up methods. Top-down methods consist of arc discharge, laser ablation and electrochemical oxidation, where the CDs are formed or “broken off” from a larger carbon structure. Bottom-up approaches include combustion/thermal routes, supported synthetic routes or microwave methods, during which the CDs are formed from molecular precursors. In general, CDs were prepared from precursors of fine carbon structures (like graphene and multi-wall carbon nanotubographite) or conventional chemicals (like carbohydrates and ammonium citrate). For the environmentally aware, some alternative renewable resources have already been successfully utilized as starting materials to prepare CDs, such as soy milk and grass. In our previous work, we reported the fabrication of CDs from chicken eggs via a rapid plasma process and from plant leaves via a pyrolysis process. Despite recent amazing advances in the fabrication of CDs, developing facile and green synthetic routes as well as broadening their practical applications are still highly needed.

Herein, we develop a new category of precursor-based CDs. Hair, a kind of natural and nontoxic raw material was used as the carbon source to produce highly fluorescent CDs by a one-step pyrolysis treatment. This strategy not only avoids the use of toxic or expensive solvents and starting materials, but also provides an effective way for reclamation of hair wastes. The as-obtained CDs exhibit excellent blue fluorescence without further surface passivation or oxidation, and show good dispersion in polymer matrices such as poly(methyl methacrylate) (PMMA) and polyvinylpyrrolidone (PVP). Based on the excellent compatibility of CDs with polymers, we embedded CDs in appropriate polymer matrix to prepare solid fluorescent macrostructured hybrids for various applications. Through microfluidic technology, we constructed one-dimensional (1D) microfiber arrays and 3D microbeads, while with the aid of inkjet printing method, we fabricated 2D patterned films. These CD-polymer fluorescent hybrid materials possess excellent overall performances, which show great potentials in such as flat panel displays and anti-counterfeiting labeling fields.

Experimental Methods

Materials

Hair was collected from local barbershop in Nanjing, which was washed by water and ethanol, and then dried for further use. Solvents including petroleum ether, n-hexane, toluene, acetone, ethanol, carbon disulfide (CS2), dichloromethane (CH2Cl2), chloroform (CHCl3) and tetrachloromethane (CCl4) were of analytical reagent grade and purchased from standard sources. Polymers including poly(methyl methacrylate) (PMMA), polyvinylpyrrolidone (PVP), polyvinyl alcohol (PVA), and...
chemicals like hydrochloric acid (HCl) and sodium hydroxide (NaOH) were also purchased from standard sources. All chemicals were used as received without further purification. Deionized water with resistance greater than 18 MΩ·cm was used in all experiments.

**Preparation of CDs**

CDs were prepared via a pyrolysis route in which hair was directly thermal decomposed at 300 °C for 2 h with a heating rate of 5 °C·min⁻¹ under nitrogen atmosphere. After cooled down to room temperature, the dark brown product was ground into finer powders in a mortar. After that, 0.01 g powder was ultrasonically dispersed in water for 20 min. Then, the suspension was centrifuged at 14,000 rpm for 10 min to remove the non-fluorescent deposit. The resultant transparent brown supernatant was further filtrated with ultra-filtration membrane (200 nm) three times to remove impurities and larger particles before characterization.

**Fabrication of Fluorescent Microbeads**

The fluorescent hybrid microbeads were fabricated via a simple microfluidic technology. The microfluidic device was assembled by inserting a capillary tube with a 30 G needle into a polydimethylsiloxane (PDMS) tube. The discontinuous phase (CD-PDMA chloroform solution) and the continuous phase (6 wt% PVA aqueous solution) were injected into the capillary tube and PDMS tube, respectively, by syringe pumps at independently adjusted flow velocities. Typically, 0.08 g PMMA was dissolved in 4 g CD-chloroform solution (CDs concentration: 3 wt%) under strong magnetic stirring to form a homogeneous solution, which served as discontinuous phase. Large droplets formed at the tip of the needle and flowed in the PDMS capillary, and we re transformed to a container. The fluorescent microbeads were obtained after chloroform evaporation at room temperature for 12 h. Finally, the fluorescent microbeads were washed with deionized water to remove residual PVA.

**Preparation of Fluorescent Microfibers**

Microfibers with fluorescence were prepared via a microfluidic spinning technology. The CDs aqueous solution (1 mg·mL⁻¹) was mixed with PVP (20 wt%) to form a homogeneous solution. And then the solution (10 mL) was introduced into the digital fluid controller, and the sample fluid volume is tightly controlled by the syringe pump device, maintaining at a flow rate of 0.1 mL·h⁻¹ under a constant voltage. To collect the alignment of the extruded fibers, they were wound around a small rotating spool fixed on a stepper motor that could horizontally move.

**Patterning from CD Solution**

The fluorescent patterns were formed via a facile silk screen printing method. The above as-prepared CD-PVP aqueous solution served as the printing “ink”. Then, the ink was quickly cast onto the printing mask, and was penetrated through the pattern screen (160 meshes) onto the paper substrate.

**Characterization**

Photoluminescence (PL) spectra were measured on a Varian Cary Eclipse spectrophotometer equipped with a Xe lamp at ambient conditions, with the excitation wavelength of 360 nm. Ultraviolet-visible (UV-vis) spectra were recorded on a Perkin-Elmer Lambda 900 UV-vis spectrometer. Fluorescence decay curve was measured based on the Leica SP5 FLIM system. Transmission electron microscopy (TEM) images of the CDs solution (1 wt%) were pictured from a JEOL JEM-2100 electron microscope. Fourier transform infrared (FT-IR) spectra were obtained on a Nicolet 6700 FT-IR spectrometer. The X-ray diffraction (XRD) pattern was conducted on a Bruker D8-ADVANCE X-ray diffractometer with Cu/Kα radiation at a scanning speed of 0.1°/min over 20 range of 10°-90°. X-ray photoelectron spectroscopy (XPS) spectra of the CDs were performed on an ESCAIB250 XPS system with Al/Kα as the source, and the energy step size was set as 0.100 eV. Raman spectrum of the CDs was gained on a Horiba HR 800 Raman system equipped with a 514.5 nm laser. Elemental analysis of the hair and the CDs was performed on an Elementar Vario EL III. Photographs of fluorescent microbeads, patterns and microfibers were observed using a Zeiss AXIO 5 Imager optical microscope.

**Results and discussion**

**Synthesis and Characterization of CDs**

In this work, CDs with blue fluorescence were successfully prepared by using natural hair as the carbon source via a one-step pyrolysis process under 300 °C for 2 h without any catalysts or further surface passivation, and their applications in fabrication of multidimensional fluorescent hybrid materials were demonstrated, as shown in Scheme 1.

The main component of hair is known as keratin, which is abundant with carbon, nitrogen and oxygen elements. Elemental analysis was performed to reveal the compositions of hair precursor and CDs derived from hair, respectively (Table 1). An obvious increase of carbon content in CDs (74.12%) was found by comparing with that of hair (61.51%), indicating that the CDs are carbon-rich material and carbonization occurs during the thermal treatment.
Table 1 Elemental analysis of the hair precursor and CDs

<table>
<thead>
<tr>
<th>Element</th>
<th>Hair</th>
<th>CDs</th>
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<tbody>
<tr>
<td>C</td>
<td>61.51 %</td>
<td>74.12 %</td>
</tr>
<tr>
<td>H</td>
<td>5.54 %</td>
<td>6.46 %</td>
</tr>
<tr>
<td>O</td>
<td>16.01 %</td>
<td>11.59 %</td>
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Fig. 1 (a) XPS spectra of hair-derived CDs and (b) the corresponding expansion of C 1s peak. (c) FT-IR spectrum and (d) Raman spectrum of hair-derived CDs.

The chemical compositions and structures of the as-prepared CDs were investigated. XPS of CDs shows the existence of carbon (C 1s, 285 eV), nitrogen (N 1s, 400 eV) and oxygen (O 1s, 532 eV; Figure 1a), which is consistent with the elemental analysis results. In the expanded image of the C 1s peak (Figure 1b), the signals at 285 eV, 286.5 eV, 288.2 eV and 289.7 eV demonstrate the presence of C=C and CH\textsubscript{x}, C=N, C=O and C=O\textsubscript{C}, and O=O functional groups. As shown in the FT-IR spectrum of CDs (Figure 1c), 3428 cm\(^{-1}\) is assigned to the OH group, 2918 cm\(^{-1}\) and 2847 cm\(^{-1}\) originate from the CH\textsubscript{2} vibrations, 1615 cm\(^{-1}\) arises from the C=O stretching, and 1384 cm\(^{-1}\) belongs to the symmetric carboxylate stretch, confirming the existence of rich -OH, -COO\textsuperscript{-} and -COOH groups on the surfaces of the CDs, which agrees well with the XPS results. An apparent G band at around 1580 cm\(^{-1}\) and a weak D band at 1350 cm\(^{-1}\) were detected in the Raman spectrum of CDs (Figure 1d), indicating the CDs are typical carbon nanomaterials. From the above results, we could draw a conclusion that the hair-derived CDs are mainly composed of sp\textsuperscript{2} graphitic carbons with some sp\textsuperscript{3} carbon defects and abundant hydroxy and carbonyl/carboxylate groups on their surfaces. Therefore, both quantum size effect and surface state of CDs could be responsible for the photoluminescence of CDs.

Optical Properties of CDs

As demonstrated in Figure 3a, the hair-derived CDs show characteristic absorption peaks centered at ~270 nm and ~330 nm in the UV–Vis absorption spectrum, which can be attributed to π-π* transition of C=C and n-π* transition of C=O, respectively. Upon UV excitation (360 nm), the CDs produce bright-blue photoluminescence in water. The corresponding PL peak is broad and centered at ~430 nm. Similar to the previous reports, the PL emission wavelength of the CDs is excitation-dependent, which red-shifts from 430 to 580 nm with increasing excitation wavelength (from 360 nm to 540 nm) (Figure 3b). The QY of the resultant CDs dispersed in water is determined to be 17.3% with quinine sulfate as a reference. We further investigated the fluorescence lifetime (τ) of the CDs by a multidimensional time-correlated single photon counting (TCSPC) to acquire further insight into the photoluminescence. The hair-derived CDs in water exhibit double exponential decay, using the Eq. (1).

\[ Y(t) = \alpha_1 \exp(-t/\tau_1) + \alpha_2 \exp(-t/\tau_2) \]  

(1)

Where \(\alpha_1\) and \(\alpha_2\) are the fractional contributions of time-resolved decay lifetime of \(\tau_1\) and \(\tau_2\). The average lifetime could be concluded from the Eq. (2).

\[ \bar{\tau} = \frac{\alpha_1 \tau_1^2 + \alpha_2 \tau_2^2}{\alpha_1 \tau_1 + \alpha_2 \tau_2} \]  

(2)

Fig. 3 (a) PL emission and UV-Vis absorption spectra of hair-derived CDs dispersed in water. (b) PL emission spectra of CDs obtained at different excitation wavelengths starting from 360 nm to 540 nm in 20 nm increments. Insert is the corresponding normalized PL spectra. (c) Fluorescence decay curves of the as-prepared hair-derived CDs dispersed in water. (d) PL intensities of hair-derived CDs in aqueous solution at different pH values.
The calculated average lifetime for the CDs is 2.83 ± 0.05 ns, which are comparable to the reported values.31, 32 Figure 3d shows the effect of different pH values on the PL intensity of the CDs in aqueous solution. The PL intensity is relatively stable in the pH range of 4-10, while decreases significantly in either a strong acidic or a strong basic solution, implying the as-prepared CDs are very sensitive to acid-base property of the solvent. This feature might be closely associated with the protonation-deprotonation of the carboxyl groups on the surfaces of the CDs.

The effect of various solvents on the PL intensity of the CDs was also investigated. We ultrasonically dispersed the CDs powders in petroleum ether, n-hexane, CS₂, CCl₄, toluene, dichloromethane, ethanol, chloroform, acetone and water under (a) daylight and (b) UV light. (c) PL emission spectra of hair-derived CDs dispersed in water, acetone, chloroform and dichloromethane. Insert is the corresponding fluorescent intensity of CDs dispersed in solvents with different polarity values.

Fig. 4 Digital photos of CDs dispersed in petroleum ether, n-hexane, CS₂, CCl₄, toluene, dichloromethane, ethanol, chloroform, acetone and water under (a) daylight and (b) UV light. (c) PL emission spectra of hair-derived CDs dispersed in water, acetone, chloroform and dichloromethane. Insert is the corresponding fluorescent intensity of CDs dispersed in solvents with different polarity values.

As shown in Figure 4b, the PL intensities enhance with the increasing solvent polarities. The CDs samples show poor fluorescence in the first five solvents, and even exhibit no fluorescent property when dispersed in petroleum ether and n-hexane, while exhibit excellent fluorescence in the latter five solvents. Figure 4c displays the fluorescent emission spectra of hair-derived CDs dispersed in dichloromethane, ethanol, chloroform, acetone and water, which can be seen that the PL intensity increases from 85 a.u. to 936 a.u., with no significant shifts of emission peaks. Insert of Figure 4c is the corresponding fluorescent intensity of CDs dispersed in solvents with different polarity values. When the solvent’s polarity is less than that of toluene, it’s unable to detect its PL spectrum by fluorescence spectrophotometer with excitation light of 380 nm at 600 eV. We contribute the main reason for this phenomenon to the large number of polar groups such as hydroxyl and carboxyl groups on the surfaces of CDs. These functional polar groups confer the CDs with different dispersibility in polar solvents, which might be responsible for the different PL intensities and is highly desirable for practical applications of the CDs. Owing to the strongest polarity of water among these solvents, CDs exhibit excellent dispersibility and PL intensity in water.

**CD-PMMA fluorescent microbeads (3D)**

Microfluidic technology has recently emerged as a powerful platform to engineer micro-/nano-materials, such as microbeads and microfibers, with easy-to-perform and wide adaptability for a variety of polymers.32-34 Figure 5a provides schematic procedure for the fabrication of fluorescent microbeads carried out in a microfluidic device. This device is made up of a PDMS capillary and an inner cylindrical 30 G steel needle. The inner steel needle was injected with CD-PMMA (3 wt%) chloroform solution, and the outer PDMS capillary was injected with 6 wt% PVA aqueous solution. The continuous phase of PVA solution broke the inner solutions at the tip of the needle, finally forming spherical droplets. After chloroform evaporation, uniform CD-PMMA fluorescent microbeads were successfully obtained.

Through adjusting the velocities of discontinuous (CD-PMMA) phase and continuous (PVA) phase, spherical droplets with different sizes can be controllable obtained. When the continuous phase velocity was fixed at 20 mL·h⁻¹, the diameter of the droplets increased from 329 µm to 436 µm with increasing discontinuous phase velocities from 1 mL·h⁻¹ to 5 mL·h⁻¹ (Figure 5b). At 3 mL·h⁻¹ for discontinuous phase velocity, when the continuous phase velocity increased from 10 mL·h⁻¹ to 50 mL·h⁻¹, the diameter of the droplets decreased from 402 to 306 µm (Figure 5c). Figures 5d-f are fluorescence microscopy images of CD-PMMA fluorescent microbeads with well monodispersity and different sizes of 329 µm, 414µm and 436µm, respectively. The microbeads exhibit bright blue and uniform fluorescence, indicating that the CDs have excellent compatibility with PMMA.

In the previous cases, the composite of semiconductor quantum dots and polymers would cause luminescence diminishing because of the detachment of the ligand from the quantum dots existing in the polymer matrices.33, 34 The hair-derived CDs herein can effectively solve the problem of compatibility with polymers, and promise a variety of applications.

Fig. 5 (a) Scheme of the fabrication route to generate fluorescent CD-PMMA microbeads. (b) A plot of microbeads diameter as a function of the flow velocity for discontinuous phase when the flow velocity for continuous phase was fixed at 20 mL·h⁻¹. (c) A plot of microbeads diameter as a function of the flow velocity for continuous phase when the flow velocity for discontinuous phase was kept at 3 mL·h⁻¹; (d-f) Fluorescence microscopy images of CD-PMMA fluorescent microbeads with different sizes (λex = 395 nm).

The CD-PMMA hybrids not only show strong PL fluorescence, but also the PL emission wavelength is excitation-dependent. Figure 6 are fluorescence microscopy images of CD-PMMA fluorescent microbeads under different excitation wavelengths. When excitation wavelengths are 395 nm, 470 nm and 546 nm, CD-PMMA hybrids emit fluorescence with wavelengths of 460 nm, 530 nm and 590 nm, respectively (Figure 6c, f, i), displaying corresponding colors as blue, green and red. The results suggest that the PL emissions red-shift accompanied with the increasing excitation wavelength. We further employed each fluorescent microbead as a single pixel unit, colorful images
can be obtained by applying an excitation backlight (letters “C” and “D” as Figure 6a, b, d, e, g, h show). These excitation-dependent multicolored fluorescent microbeads have great value and potential applications in bead panel display field.

**Fig. 6** Fluorescence microscopy images of CD-PMMA fluorescent microbeads under different excitation wavelengths: (a-b) $\lambda_{ex} = 395$ nm, (d-e) $\lambda_{ex} = 470$ nm, (g-h) $\lambda_{ex} = 546$ nm. (c, f, i) PL spectra of those corresponding fluorescent microbeads.

**CDs-PVP fluorescent microfibers (1D)**

Another indication is the fabrication of 1D microfiber arrays via microfluidic spinning technology. Figure 7a is a schematic representation of the microfluidic-spinning device. To increase the viscosity of the solution, non-fluorescent PVP was chosen as the polymer matrix to be mixed with CDs aqueous solution. The CD-PVP solution was introduced into the digital fluid controller, and the fluid volume is controlled by the syringe pump device. Using this technology, highly aligned microfiber arrays with uniform diameter (~8 µm) and homogeneous fluorescence were obtained (Figure 7b). These microfibers also have the excitation-dependent property. As shown in Figure 7, CD-PVP microfibers emit blue, green and red light, respectively, under excitation wavelength of 395 nm, 470 nm and 546 nm. Since the dimension of microfibers (1D) is lower than 2D- and 3D-structured materials, the fluorescence intensity of microfibers is lower than that of microbeads. Meanwhile, the excitation efficiency reduces with the increase of excitation wavelength, behaving that the brightness of red fluorescence (excitation by 546 nm light, Figure 7d) is distinctly lower than that of blue fluorescence (excitation by 395 nm light, Figure 7b). These uniformly fluorescent microfiber arrays benefit for a variety of applications such as optoelectronic devices.

**CDs-PVP fluorescent patterned films (2D)**

![Fig. 8](image)

Finally, we prepared CD-PVP fluorescent hybrid film, and further used CD-PVP solution as ink to fabricate fluorescent patterns. A CD-PVP film was obtained by scratching the CD-PVP aqueous solution with a coating applicator. The as-prepared film possesses good transparency (Figure 8a), and emits uniformly bright blue fluorescence under UV light (Figure 8b). Furthermore, we expanded the CD-PVP fluorescent film to versatile patterns. Silk screen printing is a useful and facile technique for creating highly defined patterns for flexible electronics and sensing. Figure 7c shows the silk screen printing process of CD-PVP solution. The colorless CD-PVP aqueous solution was applied as the printing ink, and the filter paper served as the substrate. After the CD-PVP ink penetrating from the patterned mask (160 meshes screen) onto the substrate, an anticipated pattern was immediately obtained. Remarkably, the pattern printed with CD-PVP solution is invisible under daylight (Figure 7d), but obviously visible under UV light. As shown in Figure 7e-f, fluorescent patterns of “Tai Chi” and “Chinese dragon” were observed on the filter paper substrates. The “vis-invisible” and “UV-visible” properties of CDs benefit their applications in anti-counterfeiting and labelling fields.

**Conclusions**

In summary, we successfully synthesized CDs with the use of natural hair as precursor via a facile one-step pyrolysis process. The as-prepared CDs show excellent blue fluorescence under UV and possess a quantum yield of 17 %. The functional groups on the surface of CDs confer these nanomaterials with excellent...
dispersibility in water and most polar organic solvents, as well as good compatibility with polymer matrices such as poly(methyl methacrylate) and polyvinylpyrrolidone. For practical applications, uniform fluorescent microbeads of polymer-encapsulated CDs have been prepared via a microfluidic device. The CD-PMAA microbeads show strong fluorescence, as well as multicolored emission achieved by applying different excitation light, which show great value in bead panel display applications. In addition, the fluorescent uniform microfiber arrays with ordered alignment have been fabricated via microfluidic spinning technology. Also, these CDs can be utilized as fluorescent inks for printing various luminescent patterns, whose “visible” and “UV-visible” properties promise their applications in anti-counterfeiting labeling field. Therefore, we demonstrate herein a facile strategy to prepare CDs from a natural carbon source, and further apply them to construct multidimensional fluorescent materials with versatile potential applications.

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Carbon dots are prepared via pyrolysis of natural hair, and further embedded in polymer matrix to prepare multidimensional hybrid materials.