Simple and Green Synthesis of Carbonized Polymer dots from Nylon 66 Waste Fibers and its Potential Application

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ABSTRACT: Carbonized polymer dots (CPDs) have attracted widespread attention owing to their unique properties and are usually prepared from monomers of polymers or polymers. To reduce the waste of high-value petropolymers and environmental pollution, a simple and green method for the preparation of CPDs using a hydrothermal technique based on the cross-linking enhanced emission effect was proposed, in which nylon 66 waste fibers were used as a precursor and glutaraldehyde as a cross-linking agent. The as-prepared CPDs possessed polymer/carbon hybrid structures with a 3.5 nm average diameter, and hydroxyl (\(-OH\)), carboxyl (\(-COOH\)), and amino (\(-NH_2\)) groups were present on the surface of CPDs. It can be found that the as-prepared CPDs display excitation-dependent photoluminescence emission, which is mainly attributed to the molecular state luminescence center. Because the molecular state fluorescence of CPDs could be affected by the presence of \(\text{Fe}^{3+}\) and the change of pH values, the as-prepared CPDs can be used as a probe for the detection of the concentration of \(\text{Fe}^{3+}\) and the pH variations of solution. The fluorescence intensity of CPDs was selectively quenched by \(\text{Fe}^{3+}\) in the range from 1 to 145 \(\mu\)M. In virtue of the static quenching of CPDs by \(\text{Fe}^{3+}\), a sensing system was fabricated for the quantitative detection of \(\text{Fe}^{3+}\), and its limit of detection was 0.1 \(\mu\)M. Based on the electrostatic doping/charging of CPDs, a pH sensor was fabricated. It showed that the fluorescence intensity of CPDs decreased along with the increase of pH from 2.60 to 12.6. What is more, the CPDs were found to be an alternative to traditional fluorescent inks for encryption and information storage.

1. INTRODUCTION

Carbonized polymer dots (CPDs) are novel emerging fluorescent nanomaterials, which are composed of organic polymer chains and a carbon core.\(^1,2\) CPDs are usually prepared from monomers of polymers or polymers by the process of condensation, cross-linking, or slight carbonization.\(^3-8\) Compared with traditional carbon dots, the degree of carbonization of CPDs is low and even as low as 0%. Hence, the condensation and the cross-linking process are essential for the synthesis of CPDs. Due to the specific chemical structure, CPDs have unique characteristics, such as the bright emission, high yield, and high oxygen contents ensuring excellent aqueous solubility. What is more, the polymer chain structure of the CPDs makes it possible that CPDs can be easily functionalized through blending or covalent binding with inorganic materials, polymers, and functional molecules. The functionalized CPDs could be widely used in the field of photoelectric devices, fluorescent displays, and drug delivery.\(^9\) Thus far, several papers have reported the preparation of CPDs relying on hydrothermal,\(^5,10,11\) pyrolytic,\(^12\) or microwave-assisted\(^13\) routes. However, these methods involve expensive carbon sources, post-treatment procedures, and time-consuming processes, which limit their applications. Therefore, a simple and green method for the synthesis of CPDs is still highly desired.

Nylon, which is extensively applied in the manufacture of textile fibers, engineering products, and automobile parts due to its good processability and high impact and mechanical strength, is a typical non-biodegradable polymer produced from the non-renewable and limited petroleum resource.\(^14,15\) Hence, the reuse of nylon is gaining increasing importance with the growing environmental awareness and the decrease of landfill capacity.\(^16\) Large quantities of waste fibers are generated when textile fibers, filaments, clothes, or other products of nylon are manufactured. What is more, the recycling of nylon waste fibers appears to be simple because nylon waste fibers have little or no foreign materials.

In the current study, we present a simple and green method for the preparation of CPDs using a hydrothermal technique.
based on the cross-linking enhanced emission (CEE) effect, in which nylon 66 waste fibers were adopted as a precursor and glutaraldehyde as a cross-linking agent. The as-prepared CPDs possess polymer/carbon hybrid structures with an average diameter of 3.5 nm, and there are hydroxyl (−OH), carboxyl (−COOH), and amino (−NH₂) groups on the surface of CPDs. It was found that the as-prepared CPDs display excitation-dependent photoluminescence emission, which is mainly attributed to the molecular state luminescence center. The as-prepared CPDs can be used as a probe for the detection of the concentration of Fe³⁺ and the pH variations of solution because the molecular state fluorescence of CPDs could be affected by the presence of Fe³⁺ and the change of pH values. What is more, the CPDs were found to be an alternative to traditional fluorescent inks for encryption and information storage.

2. RESULTS AND DISCUSSION

The preparation of CPDs based on the CEE effect is demonstrated in Figure 1a. Nylon 66 waste fiber was adopted as a carbon source and glutaraldehyde was used as cross-linking agent. In the process of preparing CPDs using the hydrothermal method, the cross-linking nylon 66 chains were first formed, followed by dehydration and carbonization, and then CPDs were formed. The effect of the cross-linking agent on the fluorescence intensity of CPDs was investigated, and the results are shown in Figure 1b. It can be found that the additon of glutaraldehyde can remarkably increase the fluorescence intensity of CPDs.

2.1. Morphological Characterization of CPDs. Transmission electron microscopy (TEM) and atomic force microscopy (AFM) were used to characterize the morphology of the as-prepared CPDs. As can be seen from the TEM image in Figure 2a, the shape of the as-prepared CPDs is spherical. As can be seen from the TEM image in Figure 2a, the shape of the as-prepared CPDs is spherical. The inset of Figure 2a reveals the incomplete carbonization of CPDs, which is a typical structure character. From the top inset of Figure 2a, we can see that the CPDs have a polymer structure with a lower carbonization degree, while the CPDs at the bottom of the inset of Figure 2a have a polymer/carbon hybrid structure. These results demonstrate that a lattice spacing of 0.21 nm is in agreement with the in-plane lattice spacing of graphene (100 facets) and the spacing between graphite layers (100 facets).

2.2. Structure Characterization of CPDs. X-ray photoelectron spectroscopy (XPS), Fourier transform infrared (FTIR) spectroscopy, and protonated nuclear magnetic resonance (¹H NMR) were used to characterize the as-prepared CPDs. The main reasons were they characterized the chemical structure (functional groups and chemical bonds) of the as-prepared CPDs. Figure 3a shows the survey spectrum, in which we can see three typical peaks of 284.8 eV of C 1s, 399.6 eV of N 1s, and 531.7 eV of O 1s. At the same time, the corresponding content of C, N, and O elements is 78.51, 6.94, and 14.55%, respectively. Figure 3b shows the high-resolution C 1s spectrum and three separate peaks corresponding to carbonyl carbons (C=O, 287.8 eV), sp² carbons (C=C, 284.6 eV), and sp³ carbons (C−O/C=N, 286.1 eV). Figure 3c shows a high-resolution N 1s spectrum with two peaks, corresponding to pyrolic N (400.2 eV) and pyridinic N (399.1 eV), respectively. Figure 3d shows that the O 1s band contains two peaks at 533.0 and 531.6 eV corresponding to C=O and C−O, respectively. From the XPS results, it was found that the hydroxyl (−OH) and amino (−NH₂) groups exist on the surface of CPDs. The structure of CPDs was further characterized by FTIR and ¹H NMR. Figure 3e shows the FTIR spectrum of CPDs. From the figure, we can see that the absorption peak at 3290 cm⁻¹ is the characteristic absorption peak of N−H/O−H. The absorption peak at 3060 cm⁻¹ is attributed to the N−H stretching vibrations of the secondary amide that forms a hydrogen bond. The typical peaks at 2930 and 2850 cm⁻¹ are assigned to the stretching vibration peaks of C−H. The characteristic absorption peak at 1630 cm⁻¹ is attributed to C−O stretching vibrations, and the absorption band of the
carbonyl group (C=O) in imide shows two peaks due to vibration coupling. The peak at 1280 cm\(^{-1}\) is the stretching vibration peak of secondary amide C–N. The peak at 691 cm\(^{-1}\) corresponds to the bending vibration peak of N–Ho famide. According to the results of FTIR, the surface of CPDs contains polar functional groups such as −NH\(_2\), −COOH, and −OH.\(^{15,24−28}\)

As can be seen from Figure 3f, the \(^1\)H NMR spectrum of CPDs has a peak at \(\delta = 1.50\) ppm, which proves the existence of −CH\(_2\)−. The peak at \(\delta = 2.22\) ppm is attributed to different types of fatty alcohols (OH) in the CPDs, and the peak at \(\delta = 3.15\) ppm is attributed to the presence of the −NHCH\(_2\)− group. From the above results, it can be concluded that the nitrogen element is successfully doped into the interior of CPDs, and there are hydroxyl (−OH), carboxyl (−COOH), and amino (−NH\(_2\)) groups on the surface of CPDs.

2.3. Optical Properties of CPDs. One interesting finding is that the location of the emission peak is different for different excitation wavelengths. In other words, it can be defined as excitation-dependent photoluminescence emission. The results show that the as-prepared CPDs show a significant red shift with the increase of the excitation wavelength in the range from 370 to 565 nm, which reflects the distribution of different particle sizes and the effect of varying surface states in the samples.\(^{18,29}\)

Figure 4a shows the experimental data for the fluorescence emission spectra. A large red shift (from 385 to 550 nm) with the increase of the excitation wavelength could be seen. The results obtained from the analysis of the as-prepared CPDs show that they have the most vigorous emission at 400 nm when excited by a light of wavelength of 340 nm. What is more, there is no significant change in the fluorescence intensity of the as-prepared CPDs for 7 days (Figure S1), which demonstrates the excellent stability of the CPDs. As shown in Figure 4b, the UV–vis absorption spectrum of the CPDs shows a peak at 251 nm, which is generally attributed to the \(\pi-\pi^*\) transition of the sp\(^2\) carbon structure in the CPDs. In the inset of figure (b), we can see that the CPD aqueous solution was transparent and light yellow under natural light and could emit bright blue luminescence under irradiation with a 365 nm UV light. The purpose of this experiment was to obtain the absolute fluorescence quantum yield. Its specific test conditions were that the excitation and emission slits of the fluorescence spectrometer were 4.3 and 0.43 nm, respectively. From Figure 4c, it can be seen that the absolute fluorescence quantum yield of CPDs was calculated to be 21.38% using an integrating sphere. Simultaneously, the fluorescence lifetime of the as-prepared CPDs excited by a 365 nm picosecond laser was measured using the time-correlated single-photon counting technique. According to Figure 4d, it is apparent that the fluorescence lifetime of the as-prepared CPDs at an emission wavelength of 400 nm was fitted with a double exponential fitting curve. The lifetime of the fluorescence component I and fluorescence component II was 4.42 and

Figure 3. (a) XPS full survey spectrum of CPDs; (b) high-resolution XPS spectrum of C 1s of CPDs; (c) high-resolution XPS spectrum of N 1s of CPDs; (d) high-resolution XPS spectrum of O 1s of CPDs; (e) FTIR spectrum of CPDs; and (f) \(^1\)H NMR image of CPDs.
15.88 ns, respectively, and the average lifetime was 13.57 ns according to the fit. Typically, the luminescence centers of CPDs can be roughly divided into three types: the carbon core (the quantum confinement effect or conjugated \(\pi\)-domains of the carbonized core), molecular states (the fluorescent molecules connected on the surface or interior of the carbonized core), and the surface state (hybridization of the carbon backbone and the connected chemical groups, or called the intrinsic state). The photoluminescence lifetime of the intrinsic state is about 1 ns, the photoluminescence lifetime of the carbon core is more than 4 ns, and the photoluminescence lifetime of molecular states is 10 ns. Based on this, the fluorescence component I is assigned to the carbon core, while the fluorescence component II is attributed to the molecular states. As shown in Figure 4e, the proportion of the fluorescence component (molecular state) of CPDs at an emission wavelength of 400 nm is as high as 79.84%. As can be seen from Figure 4f, the proportion of the fluorescence lifetime varies with the emission wavelength in the range of 380−460 nm, and the CPDs were excited using a 365 nm picosecond laser. The results showed the proportion of fluorescence components II is over 50% all the time, which means that the main luminescence center of the as-prepared CPDs is the molecular state. Based on the above results, the as-prepared CPDs could be used as fluorescent probes for detection purposes, and the reason is the molecular states of CPDs may be affected by the presence of metal ions and the changes in pH values.

### 2.4. Detection of Fe\(^{3+}\) with CPDs as a Fluorescent Probe

The ferric ions (Fe\(^{3+}\)) are an essential trace element in the human body, playing a vital role, especially in the growth, development, and many different metabolic processes of individual living systems. Several diseases, such as anemia, intelligence decline, heart failure, cancer, and so on, have been proved to have a close link with the abnormal concentrations of Fe\(^{3+}\). Fe\(^{3+}\) is involved in oxygen uptake as well as metabolism and intracellular oxygen transport. In a recent research study, it has been found that high levels of Fe\(^{3+}\) in the body cause certain cancer and dysfunction of specific organs (such as the heart, pancreas, and liver). Therefore, the Fe\(^{3+}\), which has a vital role in adequate intake to prevent certain diseases in human and animal health, should be detected in business applications and our daily life.

In this research, the as-prepared CPDs were designed as fluorescent probes for the detection of Fe\(^{3+}\), because of their selective quenching by Fe\(^{3+}\). In order to demonstrate the quenching ability with the addition of different metal ions (Cu\(^{2+}\), Cr\(^{3+}\), Zn\(^{2+}\), Ba\(^{2+}\), Fe\(^{3+}\), Ca\(^{2+}\), Na\(^+\), Cd\(^{2+}\), K\(^{+}\), Li\(^+\), Mg\(^{2+}\),...
Fe$^{3+}$, and Ag$^+$), the changes in fluorescence intensity (ΔF) of CPDs are shown in Figure 5a. Compared with unaffected fluorescence intensity upon addition of other metal ions (Cu$^{2+}$, Cr$^{3+}$, Zn$^{2+}$, Ba$^{2+}$, Ca$^{2+}$, Na$^+$, Cd$^{2+}$, K$^+$, Li$^+$, Mg$^{2+}$, Fe$^{2+}$, and Ag$^+$), the fluorescence intensity of the CPD solution is obviously quenched upon the addition of Fe$^{3+}$ at an excitation wavelength of 360 nm. This categorically proves that the as-prepared CPDs are ideal candidates for selective and sensitive detection of Fe$^{3+}$. Figure 5b illustrates the fluorescence emission spectra of CPD solution with different concentrations of Fe$^{3+}$ (0, 1, 5, 10, 20, 30, 40, 50, 60, 75, 100, and 145 μM). It is clear that the concentration of Fe$^{3+}$ increases with the gradual decrease of fluorescence intensity. ΔF of the CPDs is linearly dependent on concentrations of Fe$^{3+}$, which can be observed in Figure 5c. The linear regression can be defined as $ΔF = 4714 + 661C$ ($R^2 = 0.997$) with a limit of detection of 0.1 μM.

The fluorescence quenching mechanism of CPDs by Fe$^{3+}$ was studied by measuring the fluorescence lifetime of CPDs before and after quenching by Fe$^{3+}$ (100 μM). It can be found in Figure 5d that the fluorescence lifetimes of CPDs before and after quenching are the same, 13.57 and 13.46 ns, respectively. As a result, the quenching mechanism is found to be static, meaning that a coordination reaction has occurred between CPDs and Fe$^{3+}$ to form a non-fluorescent substance.

2.5. pH Detection with CPDs as a Fluorescent Probe. There is a considerable concern regarding pH changes in all walks of life, because almost all processes are reliant on pH in the chemical, biological, biochemical field. For example, soil pH is a critical factor for agricultural production. In most cases, crops healthily grow when the soil pH value is close to neutral (pH 6–7.5), because the uptake of nutrients from the soil by crops is affected by pH. Many industrial processes, such as textiles, chemicals, pharmaceuticals, and so forth, depend on pH measurements. What is more, pH is crucial in biological processes, biomedical applications, and food spoilage monitoring. As a result, the facile and accurate monitoring of pH in the environment is becoming increasingly important. Interestingly, when the fluorescence intensity of CPDs at different pH values was measured (Figure 6a), it was observed that the fluorescence intensity of CPDs decreased along with the increase of pH from 2.60 to 12.6. Based on this phenomenon, the as-prepared CPDs were used for the fabrication of a pH sensor. Specifically, the fluorescence intensity of CPDs at 400 nm decreased linearly along with the pH value ($R^2 = 0.9949$), which demonstrated that the CPDs have potential for sensing pH. The schematic illustration of the mechanism of sensing pH with CPDs as a fluorescent probe is shown in Figure 6c. When the pH of the CPD solution was changed from alkaline to acidic, the deprotonation and protonation of the carboxyl and amine groups on the surface of the CPDs cause electrostatic doping/charging of the CPDs. What is more, the fluorescence intensity of CPDs exhibited good reversibility in solution with different pH values (Figure 6d). It was found that there is no visible change in fluorescence intensity after 10 cycles from pH 4 to pH 10.8 due to the high pH reversibility of CPDs, when the pH was tuned by NaOH and HCl solutions repeatedly. The above observation further confirms that there are hydroxyl (–OH), carboxyl (–COOH), and amino (–NH$_2$) groups on the surface of CPDs.

2.6. Fluorescent Ink. Fluorescent inks are always adopted as an anticounterfeiting marker, which is invisible in visible light but becomes apparent when exposed to ultraviolet light with appropriate wavelengths. Subsequently, it can be used for multicolor barcodes to distinguish the authenticity of products and information storage. Nowadays, most commercially available fluorescent inks contain toxic chemicals, and are therefore not environmentally friendly as well as unsuitable for biological applications. CPDs are demonstrated to be a promising substitute for organic fluorescent dyes, rare-earth luminescent materials, and semiconductor quantum dots due to their properties, such as superior environmental friendliness.
and biocompatibility, excellent optical properties, and so forth. Excitation-related emission of CPDs results in different light outputs under the excitation of light with different wavelengths, which makes it harder to imitate and gives them enhanced security characteristics. The application of CPDs as the fluorescent ink was studied by printing anticounterfeit patterns on paper substrates using a HP DeskJet 2132 inkjet printer. The images of the anticounterfeit practices under UV light (365 nm) irradiation are shown in Figure 7. It was observed that the anticounterfeit patterns emit bright blue fluorescence, which could be easily distinguished with the naked eye. The two-dimensional code of WeChat official account for School of Materials Design and Engineering of Beijing Institute of Fashion Technology can be scanned and recognized with WeChat. These results indicate that CPDs can be used as fluorescent inks for encryption and information storage applications.

3. CONCLUSIONS

A simple and green method was developed for the preparation of CPDs from nylon 66 waste fibers using a hydrothermal technique, in which glutaraldehyde was employed as a crosslinking agent based on the CEE effect. The as-prepared CPDs possess polymer/carbon hybrid structures with an average diameter of 3.5 nm, and there are hydroxyl (−OH), carboxyl (−COOH), and amino (−NH2) groups on the surface of CPDs. It can be found that the as-prepared CPDs display excitation-dependent photoluminescence emission with a quantum yield of 21.38%. The fluorescence intensity of CPDs was selectively quenched by Fe3+ in the range from 1 to 145 μM. In virtue of the static quenching of CPDs by Fe3+, a sensing system was fabricated for the quantitative detection of Fe3+ whose limit of detection is 0.1 μM. Based on the electrostatic doping/charging of CPDs, a pH sensor was established. It was found that the fluorescence intensity of CPDs decreased along with the increase of pH from 2.60 to 12.6. What is more, the CPDs were found to be an alternative to traditional fluorescent inks for encryption and information storage applications.

4. MATERIALS AND METHODS

4.1. Materials. Nylon 66 waste fibers were obtained from Shanghai Different Chemical Fiber Co., Ltd. Glutaraldehyde (50% in H2O), silver nitrate, lead sulfate, agar, and soluble starch were supplied by Shanghai Aladdin Biochemical Technology Co., Ltd. Sodium chloride, zinc chloride, chromium chloride, calcium chloride, and glycerol were obtained from Beijing Tongguang Fine Chemical Co., Ltd. Barium chloride and potassium sulfate were purchased from Beijing Chemical Factory. Iron(II) chloride, cadmium nitrate, lithium chloride, copper chloride, and magnesium sulfate were provided by Tianjin Fuchen Chemical Reagent Co., Ltd. Iron(III) chloride was purchased from Sinopharm Chemical Reagent Co., Ltd.

4.2. Apparatus. For characterizing the morphology and size of the as-prepared CPDs, a transmission electron microscope (model JEM-2100F, Japan Electron Optics Laboratory Ltd.) and an atomic force microscope (Dimension Icon, Bruker Corporation) were employed. A Thermo Fisher Scientific ESCALAB 250XI spectrometer with a monochromatic X-ray Al Kα excitation source (1486.6 eV) was used for XPS characterization of the as-prepared CPDs, and binding energies were calibrated based on the C 1s spectrum at 284.8 eV. A multichannel fluorescence spectrophotometer [FS5 from Techcomp (China) Ltd.] was used to obtain the UV–vis
absorption and fluorescence spectra, as well as the fluorescence quantum yield.

4.3. Synthesis of CPDs with a One-Step Hydrothermal Method. In this study, CPDs were prepared using a hydrothermal method with nylon 66 waste fibers as precursors and glutaraldehyde as a cross-linking agent. The specific preparation procedure was that nylon 66 waste fibers, glutaraldehyde, and ultrapure water were added in a 50 mL polyphenylene-lined stainless-steel autoclave in a certain proportion. Then, the autoclave was kept at a particular temperature in a drying oven for a specific time.

4.4. Quantitative Detection of Fe³⁺. 20 μL of the as-prepared CPD solution and 1.98 mL of the aqueous solution containing different concentrations of Fe³⁺ were added to a four-way fluorescent colorimetric dish using a pipetting gun. Then, the fluorescence spectrum was measured after mixing once for 1 min thoroughly. The specific parameters are as follows: the excitation wavelength is 340 nm, the emission wavelength is measured in the range of 350–480 nm, and the slit widths are 1 and 2 nm. Following that, a linear relationship between ΔF and the concentration of Fe³⁺ in aqueous solution was established. The fluorescence intensity at the emission peak of CPDs in aqueous solution without Fe³⁺ was recorded as F₀. In contrast, the fluorescence intensity at the emission peak of different amounts of Fe³⁺ in aqueous solution was recorded as Fᵣ and the difference between F₀ and Fᵣ was recorded as ΔF.

4.5. Application of CPDs in pH Measurements. First, 1 mL of the as-prepared CPD solution was added to 100 mL water to obtain a mixture solution. Second, the mixture solution with different pH values (2.6, 3.6, 4.7, 5.6, 6.6, 7.5, 8.6, 9.7, 10.7, 11.6, and 12.6) was obtained by adding HCl and NaOH. Then, the fluorescence emission spectra excited by the light with a wavelength of 340 nm were recorded in the range of 350–480 nm. At last, the fluorescence intensities of CPDs at 400 nm were measured to evaluate the pH values of the solution. All the above measurements were repeated three times, and the standard deviation was calculated as the error bar.

4.6. Fluorescent Ink Evaluation. Recently, there has been growing interest in fluorescent ink. It is an essential component in the security field. In this study, 0.1 g of CPDs was dispersed in 8 mL ethanol and glycercin (2 mL) to prepare a fluorescent ink. CPDs’ anticounterfeit patterns were printed on paper substrates using a HP DeskJet 2132 inkjet printer, and the printed patterns were observed and photographed under a 365 nm ultraviolet lamp.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c04808.

Time-dependent fluorescence intensity of the as-prepared CPDs (PDF)

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Notes

The authors declare no competing financial interest.

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