One-step solvothermal synthesis of red emissive carbonized polymer dots for latent fingerprint imaging

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ABSTRACT

Photoluminescent carbon-based nanomaterials (CNMs) have attracted much attention over the past decade due to their unique optical characteristics and negligible toxicity. However, it is very difficult to obtain red emission of CNMs. Bright red fluorescent carbonized polymer dots (CPDs) were prepared by facilely adjusting the reaction temperature through a one-step solvothermal route, using *p*-phenylenediamine (PPD) as precursor. The as-synthesized CPDs exhibit excitation-independent emission at about 608 nm under excitation from 365 to 550 nm. Loading CPDs in starch to form CPDs–starch powder, the resultant powder exhibits strong red emission and the typical aggregation-induced fluorescence quenching was effectively suppressed, thus allowing the CPDs to be used in solid state form. More importantly, latent fingerprints (LFPs) on surfaces of various substrates, including glass, stainless steel, marble, adhesive tape, aluminum foil, painted wood, compact disc (CD), and coin, are developed by CPDs–starch powder and exhibit clear patterns and satisfactory ridge details under a 365 nm UV lamp. Furthermore, fingerprints on surfaces with multicolored background and strong florescent properties could also be clearly observed. These results suggest that CPDs–starch powder can be used as a fluorescent labeling agent for the visualization of LFPs in forensic science.

1. Introduction

Fluorescent carbon-based nanomaterials (CNMs) including carbon nanoparticles, graphene quantum dots, and carbon dots (CDs), have attracted increasing attention due to their superior optical properties, high stability, low toxicity, excellent photoinduced electron transfer properties, and simple synthetic routes [1–3]. These characteristics make CNMs useful in a variety of applications, such as in bioimaging [4,5], light-emitting devices [6], photocatalysis [7], and so on. At present, various synthesis methods have been developed to prepare CNMs, including electrochemical oxidation, microwave synthesis, ultrasonic processing, thermal decomposition, and hydrothermal/solvothermal synthesis strategies [8], etc. Meanwhile, organic molecules [9] and natural products [10] are successfully used as carbon precursors to prepare CNMs. The majority of current CNMs to date show intense blue light to green light emission under the excitation of ultraviolet (UV) light. However, synthesis of red fluorescent CNMs is very challenging, and lack of red-emitting CNMs greatly impedes their development and widespread applications.

To achieve red-emissive CDs, several methods have been developed, including surface state controlled by synthetic routes [11], element doping [12], using proper materials [13], and surface modification [14], etc. Ding et al. reported that multicolor emissive CDs were prepared through a hydrothermal method followed by column separation, used *p*-phenylenediamine and urea as starting materials [15]. Under 365 nm UV light excitation, these separated CDs emitted bright and stable emission in gradient colors from blue to red. The different emission colors were attributed to the different surface states. Miao et al. synthesized S, N codoped CDs using citric acid and thiourea as precursor by hydrothermal method [16]. Because of doping effect of S and N elements, the resulting CDs showed red emission at 594 nm with excitation at 560 nm. Jiang et al. fabricated red, green, and blue emission CDs using three isomers of phenylenediamine as precursor through a solvothermal process [17]. Through solvothermal treatment of citric acid and ethylenediamine in formamide solution, Ding et al. synthesized red-emitting CDs with emission peak at 627 nm when excited at 560 nm [18]. Experimental alteration and adjustment of surface chemistry of CDs with suitable functional groups have also been proved to be efficient ways to obtain red fluorescent CDs [19]. Despite huge efforts have been made to fabricate red-emissive CDs, the preparations

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involve complicated separation/purification process. Therefore, developing facile and controllable process to prepare CNMs with bright red emission is still highly desirable.

The developed red emissive CNMs can be used for fingerprint imaging which is useful for personal identification in forensic investigations. Most fingerprints deposited at crime scenes are invisible to naked eyes and are called latent fingerprints (LFPs). Various efforts by researchers in the development of new fluorescent reagents and methods for developing LFPs more efficiently have appeared [20,21]. Recently, available luminescent nanoparticles, especially rare earth fluorescent nanomaterials have been successfully used for the detection of LFP$_S$ [22–24]. CNMs, as one type of cost-effective, highly luminescent-stable, environmentally friendly nanomaterials, are also expected to be applied for the visualization of LFP$_S$ [25,26].

Here, we present a simple synthetic strategy to prepare red-emissive carbonized polymer dots (CPDs) by one-step solvothermal treatment of *p*-phenylenediamine using toluene as solvent, which is carried out without any separation and purification process. By dispersing CPDs into starch matrix to prevent the fluorescence from quenching, this yielded powder produces bright red emission under 365 nm UV light excitation. The potential application of CPDs–starch powder for developing LFPs is explored. The results indicated that CPDs–starch powder can be employed as luminescent probes for imaging of LFPs with enhanced contrast, better selectivity, and low background interference on various surfaces.

2. Experimental

2.1. Materials

p-Phenylenediamine (PPD, 99.9%), toluene, ethanol and starch obtained from Sinopharm Chemical Reagent Co. (China) were all of analytical grade.

2.2. Characterization

XRD measurement was performed on an X'Pert Pro diffractometer (PANalytical Co., Holland) with Cu Kα radiation. The morphology of sample was observed by a JEM-2100 transmission electron microscope (TEM) operating at 200 kV (JEOL, Japan). Fourier transform infrared (FT-IR) spectroscopy was obtained on a Spectrum One FTIR spectrometer with the KBr pellet method (PerkinElmer, USA). X-ray photoelectron spectroscopy (XPS) measurements were recorded by the ESCALAB250 surface analysis system (Thermo VG Company, USA). The UV–vis absorption spectra were carried out on a UV-2100 spectrometer (Ruili, China). Fluorescence emission and excitation spectra were measured on an F-4600 spectrophotometer (Hitachi, Japan).

2.3. Preparation of CPDs

CPDs were prepared by a one-step solvothermal method. Briefly, 0.20 g of *p*-phenylenediamine (PPD) was mixed with 20 mL of toluene within a Teflon-lined autoclave and then heated at 160 °C for 10 h in a constant temperature drying oven. After cooling down to room temperature, the crimson supernatant was discarded and the solids in the bottom of the autoclave were collected carefully and washed with toluene several times. For simplicity, the CPDs prepared at different reaction temperatures were denoted as CPDs-160, CPDs-180, and CPDs-210, respectively.

2.4. Preparation of CPDs powder

10 mg of CPDs was dissolved in 10 ml of ethanol to form a clear solution. Then, 1 g starch was added to the above solution with ultrasonic treatment and dried overnight under ambient circumstances to get a composite powder for red emission. The sample was denoted as
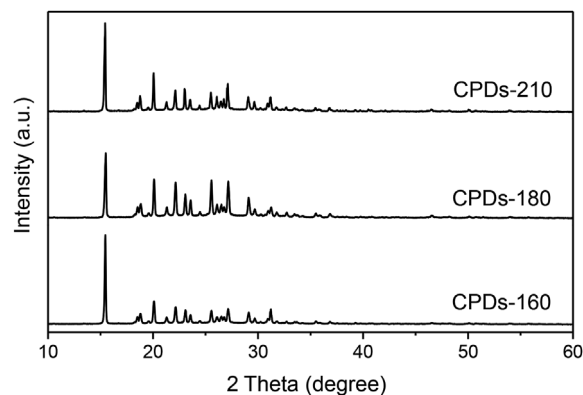

Fig. 1. The X-ray powder diffraction (XRD) patterns of the different CPDs samples.

CPDs-starch.

2.5. Fingerprint detection

LFPs were collected from volunteers by lightly wiping fingers across forehead and then pressing fingers on a chosen substrate surfaces. To develop LFPs, CPDs-starch powder was dusted on the surface of substances followed by a light brushing action to eliminate excess powder. The developed LFPs were recorded with a Canon EOS 500D digital camera under UV 365 nm light.

3. Results and discussion

Fig. 1 shows the XRD patterns of the various CPDs samples. The presence of sharp and intense diffraction peaks revealed a highly ordered and crystalline structure of CPDs [11]. The X-ray data of obtained CPDs samples presents identical crystalline peaks, demonstrating that PPD can produce the process of successive polymerization and carbonization at the temperature range of 210 to 160 °C [27].

TEM image of as-prepared CPDs-160 is shown in Fig. 2, which displays monodispersed carbon nanoparticles with average sizes about 12.5 nm.

FT-IR analysis was carried out to characterize the functional groups on CPDs-160 surface (Fig. 3A). As shown in Fig. 3A, absorption peaks at the region of 3408–3201 cm^{-1} were assigned to stretching vibrations of
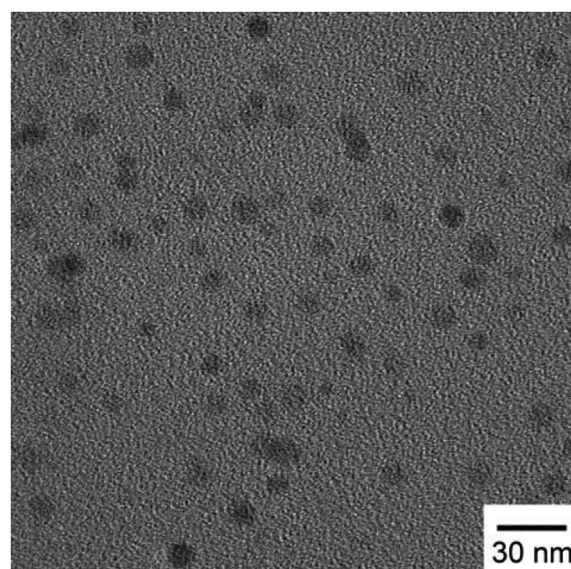

Fig. 2. TEM image of as-prepared CPDs-160.