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Synthesis and properties of fluorescent CQDs/PLA 3D printing composites based on waste rice noodles

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Abstract: *Fluorescent carbon quantum dots (CQDs) were hydrothermal synthesized with waste Guilin rice noodles as raw materials. By blending the resulted CQDs with polylactic acid (PLA), fluorescent CQDs/PLA composites was obtained and used for 3D printing. The 3D printing products of the CQDs/PLA composites display blue fluorescence which could be specifically quenching with the existence of* Fe^{3+} *ions. Therefore, the 3D printing sensor of CQDs/PLA composites could be used for* Fe^{3+} *detection, with a good linearity in the range of* 1×10^{-4}–6×10^{-4}*mol/L and a lowest limit of detection of* 9.61×10^{-5} *mol/L. In addtion, the resulted 3D printed* Fe^{3+} *sensor could achieve stability and repeated usage.*

Keywords: *waste rice noodles, CQDs/PLA 3D printing composite, fluorescence quenching,* Fe^{3+} *detection*

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I. Introduction

Due to many advantages such as excellent water solubility, chemical stability and photobleaching resistance, carbon quantum dots (CQDs) has attracted considerable attention of researchers and showed potential applications in photocatalysis, sensor, printing ink, surfacing engineering, fluorescence biological imaging, and etc[1-4]. Detection of iron (Fe) ion is one of the research hotspots in multifarious applications of CQDs, for iron plays a critical role in growth and development of organism. It has been reported that CQDs prepared with biomass carbon sources like poplar leaves[5], lemon juice[6], pear juice[7], corncob[8], and alkali lignin[9] all can be used to detect iron ions. By now, CQDs solution is still the main carrier in detection operation of metal ions, The testers can simplely mix the CQDs solution and the test sample, and then test their fluorescence quenching. However, the CQDs solution is not portable and esay to reused, it also can not be stored for a long time. Thus, it is nessary to explore new existence form of CQDs for detecting metal ions

Among multifarious carbon sources which can be used for CQDs' preparation, cooking waste is a kind of biomass resource with strong biodegradability. Synthesis of CQDs with cooking waste as raw material can reduce the amount of organic matter entering the landfill, the generation of odor and landfill leachate, which can obtain double benefits of energy and environmental protection[10-11]. For example, Milrad et al reported the synthesis of blue fluorescent CQDs by using ice-biryani from kitchen waste as raw material, and the resulted CQDs displayed a small size range of 2-5 nm and a good quantum yield of 41%[12]. On the other hand, Guilin rice noodle is a traditional snack and locals' daily diet in Guilin city, China, and a large number (about 70 tons) of surplus waste rice noodles are produced every day. Nevertheless, most of the waste rice noodles are used as raw material of low-margin fermented feed, and the others are abandoned directly, which may cause the potential and long-term pollution to the soil and aqueous environment. Thus, it is nessary to explore an effective way for recycling waste rice noodles. The main organic constituent of waste Guilin rice noodles is starch (more than 70% at weight in dehydrated waste Guilin rice noodles), which implys that waste Guilin rice noodles may be carbonized in hydrothermal condition and form fluorescent CQDs.

It is well known that 3D printing is an effective method for rapid individual production[13]. As one of the most popular molding technology of 3D printing, fused deposition molding (FDM) can produce fabric like solid state products, which can allow the osmosis of metal ions and small molecules[14]. Thus, by using a 3D printing composites contained sensors like fluorescent CQDs, it is expected to design and printed a kind of device for metal ions' detection. Thus, in order to recovery waste rice noodles effectivelly and design new functional 3D printing composites, we prepared CQDs with waste Guilin rice noodles as raw materials and blended them with polylactic acid (PLA), synthesized a fluorescent CQDs/PLA 3D printing composite, and investigate its fluorescent properties and appliction for Fe^{3+} detection.

II. Experimental Section

2.1 Materials and methods

The polylactic Acid (PLA, 6202D, powder) with a density of 1.24g/cm^3 and a molecular weight of 300000~320000g/mol was purchased from NatureWorks LLC, USA. The waste Guilin rice noodle (main constituent: Starch 21.36g/100g; Protein 1.91g/100g; Fat 0.4g/100g; Water 76.33g/100g) was collect from the canteen of Guilin university of technology.

2.2 Preparation and 3D printing of CQDs/PLA 3D printing composites

10 g waste Guilin rice noodles were grinded to a smooth paste in a mortar, and then mixed with 20 g deionized water. The resulted mixture were transfered to a 50ml sealed Teflon-lined autoclave, and then heated at 200 °C for 10 hours. After natural cooling, the liquid part was filtered and dialyzed in dark for 24 hours, resulting fluorescent CQDs water solution (concentration of CQDs: 45mg/100mL). Then, 4 mL CQDs solution was mixed with 50 g PLA and dried overnight at 50 °C. The resulted CQDs/PLA mixture was added to a XinShuo WSJXT-12 miniature single screw extruder, with a feed inlet temperature of 70 °C, a screw area temperature of 160 °C and a discharge outlet temperature of 80 °C. The semi-molten CQDs/PLA composite was extruded from the discharge port, drawn through the circulating water cooling tank and then introduced into the silk collector. When the screw speed, traction speed and silk collector speed were adjusted to 42 rpm, 170 rpm and 7 rpm respectively, transparent 3D printing wires of CQDs/PLA composite with a diameter of 1.75 mm ± 0.1 mm were obtained (See Figure 1a).

3D printing of CQDs/PLA 3D printing composite was carried out in a JG-Maker A3 FDM 3D printer, with a extrusion head temperature of 200 °C, a bed temperature of 50 °C and a printing speed of 50 mm/s. The 3D printed product was a kind of Near colorless and transparent solid (See Figure 1b).

2.3 Characterization

The Infrared (IR) spectrum was recorded as KBr pellets at a range of 400-4000cm^{-1} on a Nicolet 5700 FT-IR spectrometer with a spectral resolution of 4.00 cm^{-1}. The morphologies of resulted CQDs were characterized by using JEM-2100F field emission transmission electron microscope (TEM).

The photoluminescence spectra and Fe^{3+} detection were examined with a Varian fluorescence spectrophotometer with a xenon lamp as the excitation source in the range of 380–720 nm and a excitation wavelength of 340 nm. In Fe^{3+} detection, 3D printed device of CQDs/PLA composite could be directly pluged into the sample solution, and the existence and concentration of Fe^{3+} could be tested by the fluorescence quenching degree of the CQDs/PLA device.

III. Result And Discussion

3.1 Structural characterization of CQDs based on waste rice noodles

As shown in Figure 2a and 2b, CQDs synthesized by waste Guilin rice noodles showed a regular spherical morphology. Its particle size was mainly distributed between 1.5-2.5nm, which was well dispersed and barely reunited. The IR spectrum of CQDs (Figure 2c) indicate that there were hydroxyl and amino fuctional groups, whose stretching vibrations and bending vibrations were located at about 3424cm^{-1} and 1629cm^{-1}, respectively. The absorption peak at 1709cm^{-1} revealed the existence of carboxyl group. Those polar group in the surface of the CQDs might play an importance role in Fe^{3+} detection.

3.2 Fluorescent properties and Fe^{3+} detection of CQDs/PLA 3D printing composite based on waste rice noodles

As shown in Figure 3a, 3D printed device of CQDs/PLA composite showed blue fluorescence with an emission peak at 423 nm when pluged into distilled water. In liquid samples contained Fe^{3+}, evidently fluorescence quenching was observed in the 3D printed device, and its fluorescence intensity decreased with the increasing of Fe^{3+} concentration. Moreover, among 15 different metal ions (Pb^{2+}, Al^{3+}, Fe^{3+}, Ba^{2+}, Co^{2+}, Cu^{2+}, Mn^{2+}, Ni^{2+}, Zn^{2+}, Cr^{3+}, Mg^{2+}, Hg^{2+}, Ca^{2+}, Ag^{2+} and Cd^{3+}), only Fe^{3+} could display specific fluorescence quenching, while the other metal ions had relatively little effect on fluorescence intensity of CQDs/PLA device (See Figure 3b). Therefore, 3D printed device of CQDs/PLA composite could recognize and detect Fe^{3+} in aqueous solution with high selectively.

In Fe^{3+} solution with a concentration range from 1×10^{-4}–6×10^{-4} mol/L, the fluorescence response (F/F_0) of CQDs/PLA device was linearly correlation with Fe^{3+} concentration. After fitting, a linear equation could be obtianed, in which F/F_0 =0.972-605.58C_{Fe}, with R_2 = 0.99087, and the lowest limit of detection for quantitative analysis was calculated to be 9.61×10^{-5} mol/L. Thus, 3D printed device of CQDs/PLA composite had potential applications in quantitative analysis of Fe^{3+} (See Figure 3c).

Compared with traditional CQDs solution, CQDs/PLA 3D printing composite could produce Fe^{3+} detection device in any shape, it also displayed good stability and repeated usage. As shown in Figure 4a, the fluorescence intensity of 3D printed CQDs/PLA Fe^{3+} sensor only slightly decreased after placing at room temperature for 81 days. On the other hand, the CQDs/PLA device could be reusable by washed with distilled water, wiped and dried after Fe^{3+} detection, whose fluorescent properties barely changed after 100 working cycles (See Figure 4b).

IV. Conclusion

In this paper, we designed and synthesized a fluorescent CQDs/PLA 3D printing composite, in which the CQDs were hydrothermal synthesized with waste Guilin rice noodles as raw materials. The resulted CQDs/PLA 3D printing composite could be used for produce Fe^{3+} sensor, which could be a simple methods for the quantitative determination of Fe^{3+}. Compared with traditional CQDs solution, CQDs/PLA sensor is more portable, reuseable and can be stored for a long time. In addition, the CQDs/PLA 3D printing composites based on waste rice noodles has a higher added value than that of fermented feed, which could be advantageous for recycling waste rice noodles.

Acknowledgements

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Figures And Tables

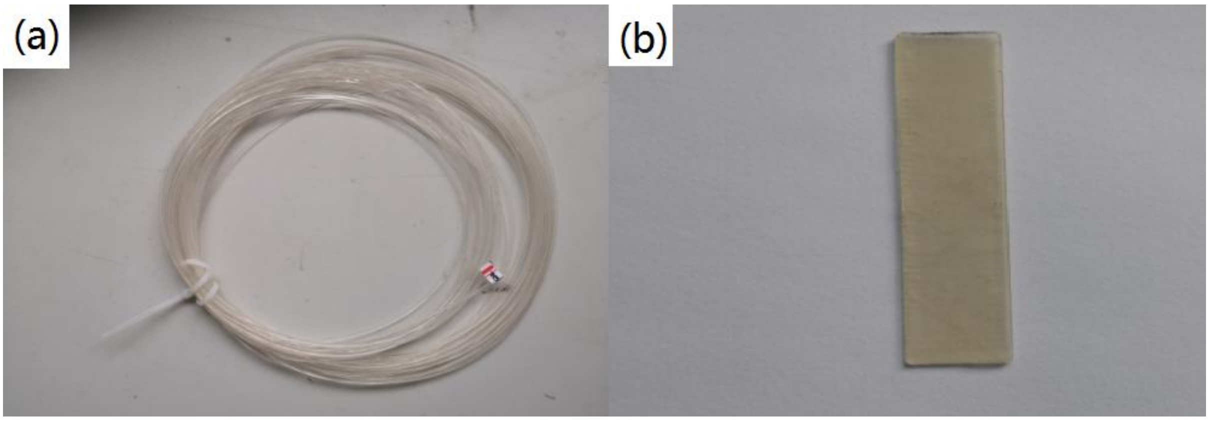

Figure 1. Photos of 3D printing wires (a) and 3D printed device for Fe^{3+} detection (b) of CQDs/PLA composite

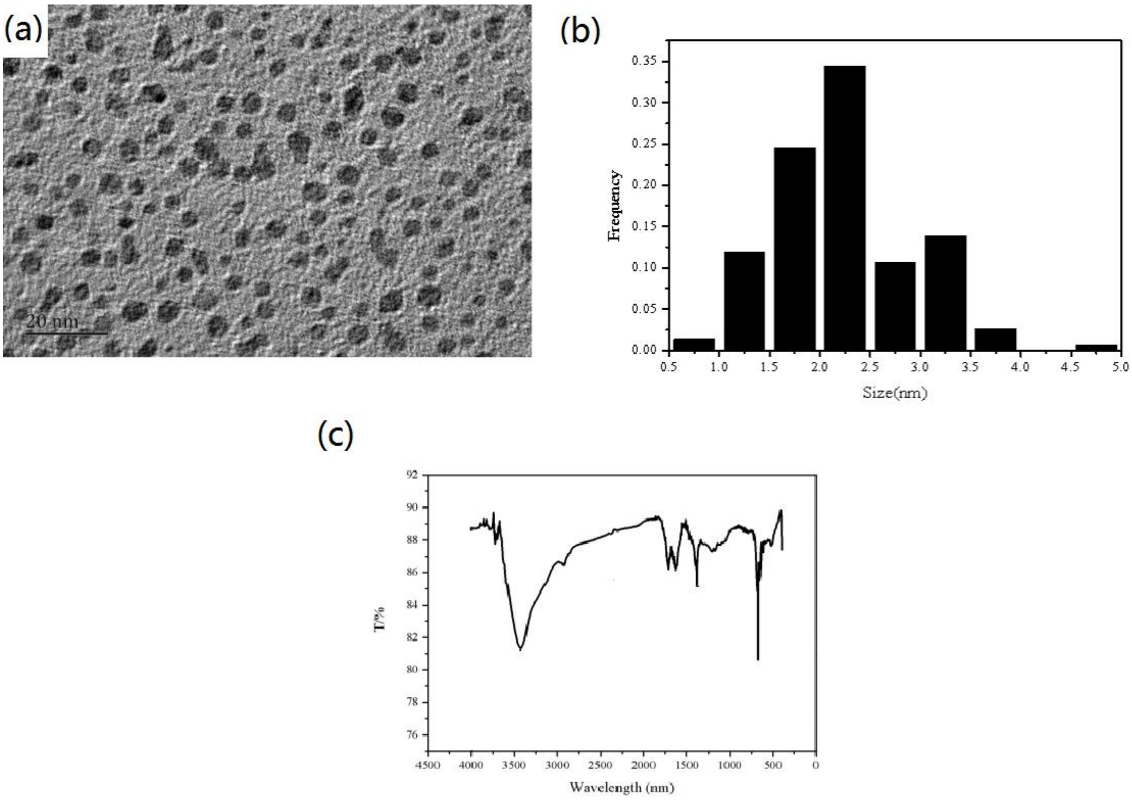

Figure 2 The TEM image (a), particle size distribution (b) and IR spectrum (c) of CQDs based on waste rice noodles

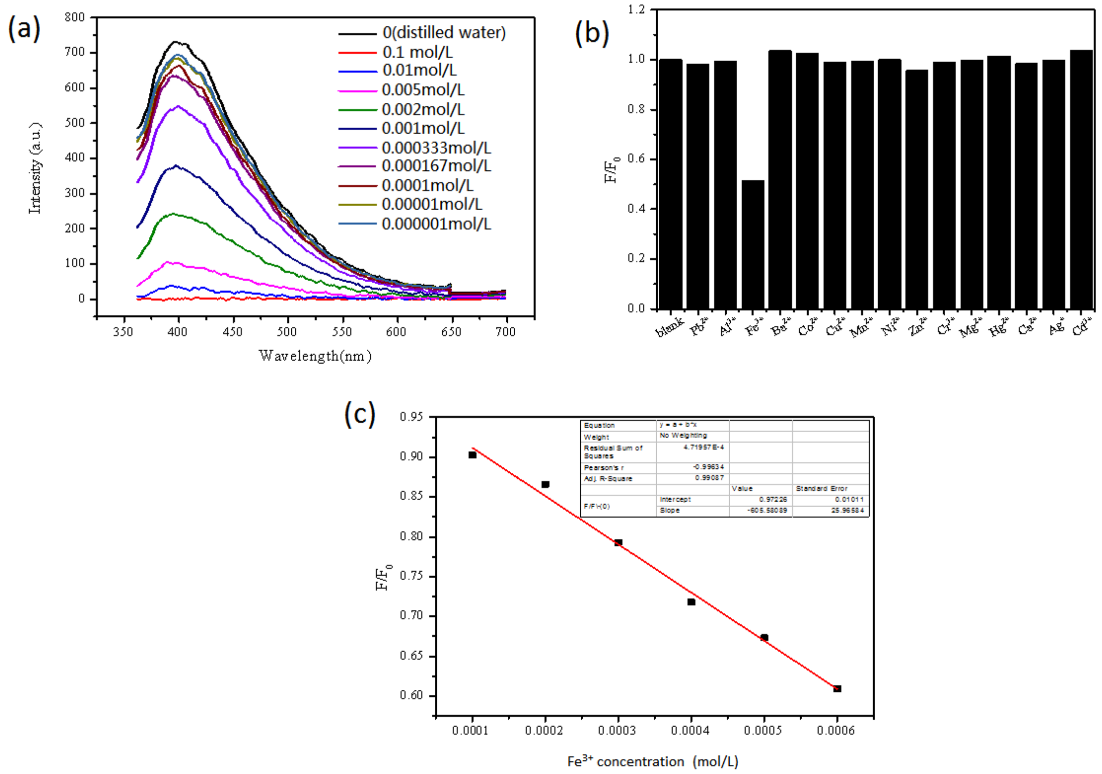

Figure 3 (a) Fluorescence spectra of 3D printed device of CQDs/PLA composite with differen concentrations of Fe^{3+}; (b) Fluorescence response of 15 metal ions to 3D printed device of CQDs/PLA composite, all concentrations of the metal ions were 10^{-3}mol/L; (c) The linear relationship between the fluorescence response (F/F_0) of CQDs/PLA device with Fe^{3+} concentration

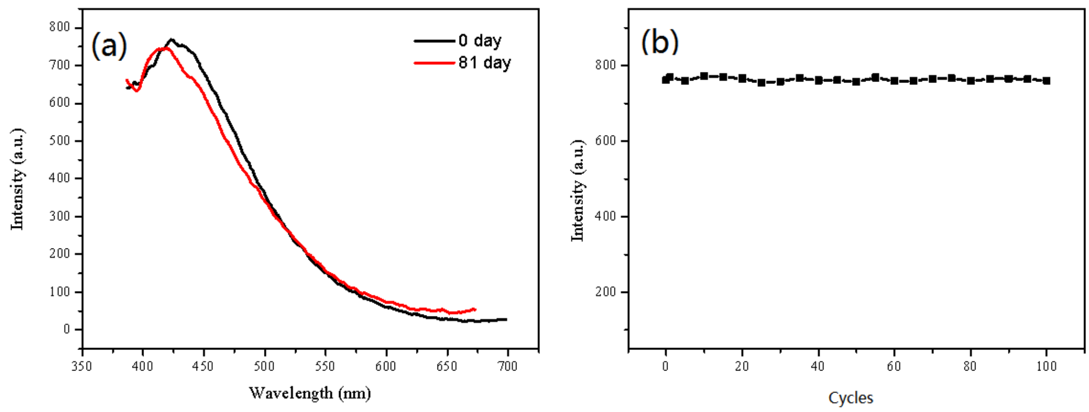

Figure 4 (a) Fluorescence spectra of 3D printed device of CQDs/PLA composite placed in different times; (b) Fluorescence intensty (423 nm) of 3D printed device of CQDs/PLA composite after different working cycles

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