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Original Article

Green Emission Carbon Quantum Dots from Lemon Juice for Selective Detection of Fe $^{3+}$ Ions

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Abstract: In this article carbon quantum dots (Cdots) were prepared by a facile, green, economical hydrothermal method of the mixed deionized water and lemon juice. Optical and structural properties of the Cdots have been extensively studied by UV–visible and fluorescence spectroscopy, x-ray diffraction (XRD) techniques, and high-resolution TEM (HR-TEM). Surface functionality of Cdots has been illustrated by Fourier transform infrared spectroscopy (FTIR). The fabricated Cdots emit bright green light with a broad spectrum. The Cdots exhibit captivating sensitivity and selectivity toward Fe $^{3+}$ with a linear range from 0 to 80 ppm and a detection limit of 38.08 ppm.

Keywords: Carbon quantum dots, lemon juice, sensing Fe^{3+}.

1. Introduction

Carbon quantum dots (Cdots) have attracted special attention of scientists because of their unique optical and chemical properties. Unlike traditional dye and semiconductor quantum dots (QDs), traditional Cdots have stable optical properties, good biodegradability and low toxicity. This material attracts attention in areas such as the biological label, photocatalysis, sensing and biomedical area [1]. Cdots are carbon nanomaterial of size less than 10 nm and considered as composed of crystalline or

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amorphous cores with predominant carbon sp^2 and abundant functional groups in the shell. During the past few years, much progress has been achieved in the synthesis, properties, and applications of Cdots. The raw carbon sources for the synthesis of Cdots can be man-made materials such as candle soot [2], graphite [3], etc. Nature provides us with an almost limitless supply of sources to develop new materials. Actually, compared with artificial carbon sources, natural products have many advantages for the synthesis of Cdots, including cost-effective and mass production. In addition, natural products that contain N, S are very suitable raw materials for the preparation of N, S-doped Cdots, without the requirement of the external addition of N/S-containing compounds [4]. In comparison with artificial sources, some natural products can be used to synthesize Cdots by more simple methods. Hydrothermal carbonization is a low-cost, environmentally friendly, and non-toxic method that has been used to prepare novel carbon materials from food products such as orange juice [5], carrot juice [6], apple juice [7], etc. Lemon is a citrus plant, very familiar to everyone because it has many uses, many benefits in everyday life. Lemon juice is used as a beverage, seasoning, decorating food or raw material in the food industry (candy, jam). In medicine, lemon juice not only helps quench the thirst but also stimulates the liver function, the kidneys work to detoxify the body, strengthen the immune system and reduce the effects of free radicals. Lemon is quite easy to grow and grows all year round, so its price is quite low. From the above benefits, we have chosen lemon juice as the precursor to prepare carbon quantum dots.

With the rapid development of the industry, concerns about environmental pollution are increasing. Iron in water often exists in the form of ions. Water with high iron content can degrade food, change the color and taste, and prevent absorption food. Therefore, the development of a method for the trace detection of Fe3+ is very important in the analysis field and environment applications. More recent studies reported that Fe^{3+} ions in water could be analyzed using luminescent Cdots that synthesized from hydrothermal treatment of citric acid [8], dopamine [9], sodium citrate [10], 2,5-diaminobenzene-sulfonic [11], L-glutamate [12] and kitchen wastes [13]. This study proposes a method for detections of Fe^{3+} ions using lemon derived Cdots. The microstructure of the Cdots was characterized by X-ray diffraction and high-resolution transmission electron microscope (HR-TEM), respectively. The fluorescent properties of the Cdots were determined by photoluminescence spectrometer.

2. Experimental procedure

Lemon was purchase in a local supermarket. A mixture of lemon juice and deionized water was transferred into a hydrothermal reactor. The reactor was then operated at 240 ℃ for 12 h and cooled naturally before opening. The obtained dark brownish solution was filtered by a filter paper to eliminate scorched solids. For metal ion analysis, the as-prepared Cdots were then mixed with various metal ion solutions (concentration 100 ppm). The metal ions were prepared in deionized water from the respective analytical grade salts (99.99% purity) of $ErCl_2.6H_2O$ (Sigma-Aldrich, St Louis, MO, USA), $FeCl_2.4H_2O$, $FeCl_3.6H_2O$, $Ca(NO_3)_2.4H_2O$, $CoCl_2.6H_2O$, KCl, $MgSO_4.7H_2O$, $MnCl_2.4H_2O$, NaCl, $NiCl_2.6H_2O$, $Ce(NO_3)_3.6H_2O$ which were purchased from Merck (Darmstadt, Germany). The photoluminescence (PL) spectra of the Cdots were obtained using a NANO LOG spectrofluorometer (Horiba, Edison, NJ, USA) equipped with a 450 W xenon arc lamp. Ultraviolet-visible (UV–vis) absorption spectra were analyzed by Cary 500 spectrophotometer. The microstructure of the Cdots was determined by high transmission electron microscopy (HRTEM), JEM 2100, JEOL Techniques, Tokyo, Japan. Chemical bonding of the Cdots was measured with infrared absorption spectra (FTIR

using a Perkin–Elmer Spectrum BX spectrometer) using KBr pellets. The phase of Cdots was performed by X-ray diffraction (D8 Advance, Bruker, Bremen, Germany).

3. Results and discussions

No fluorescence was detected from the lemon juice. But after the hydrothermal process, as-obtained Cdots can emit bright green light (Fig. 1). This result indicated the essential role of hydrothermal treatment for preparation of Cdots.

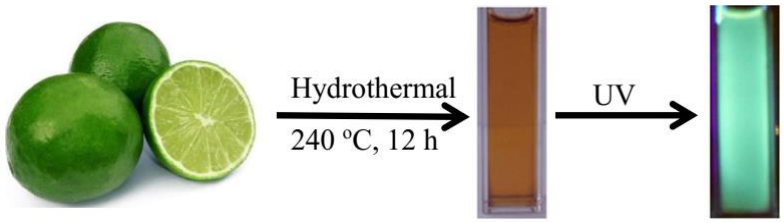

Fig. 1. Schematic illustration of the preparation of as-obtained Cdots.

The main constituents of apple juice are carbohydrates such as glucose, sucrose, fructose, citric acid, and ascorbic acid. The mechanism for the synthesis of carbon quantum dots from lemon juice involves carbonization of its constituents. In the first stage of the reaction when the temperature rises, the collisions between molecular become more intense. Dehydration and condensation occur between these functional groups resulting in the formation of long chain molecules. As lemon has weak acids such as citric, ascorbic acids, dehydration and decomposition are controlled. The process of polymerization and condensation of these products produces soluble polymers. When the concentration of aromatic clusters is large enough, nucleation occurs and carbon quantum dots are formed. Although many researchers have demonstrated the existence of crystalline sp^2-carbon-containing sections, most natural products derived Cdots have poor crystallinity. Figure 2 is an X-ray diffraction pattern of the resultant Cdots. A broad diffraction peak centered at around 20.7°, indicating the amorphous nature of Cdots.

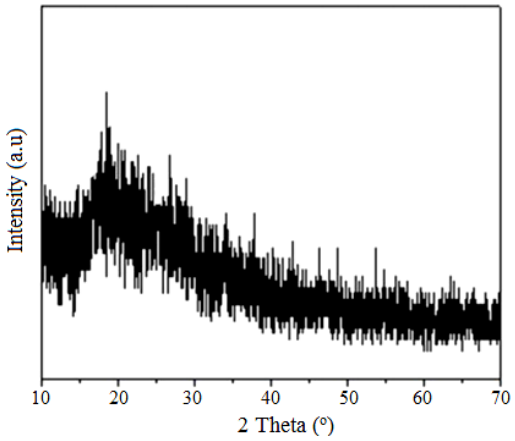

Fig. 2. X-ray pattern of Cdots.

As shown in Fig. 3, the HR-TEM image illustrated that the typical product contained a lot of well-dispersed spherical particles with the diameters about 5 nm.

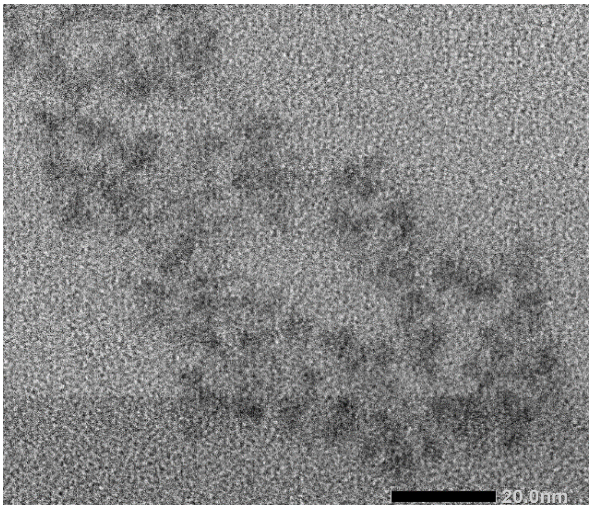

Fig. 3. HR-TEM image of Cdots.

Figure 4 is UV-Vis absorption and emission spectrum of the as-prepared Cdots.

There is an obvious peak located at 283 nm, which probably originated from the π-π* transition of the conjugated C=C bond [7]. A maximum PL emission is obtained at an emission wavelength of 515 nm with excitation wavelength at 420 nm. The green emission band originates from the surface C=O group of the Cdots [14].

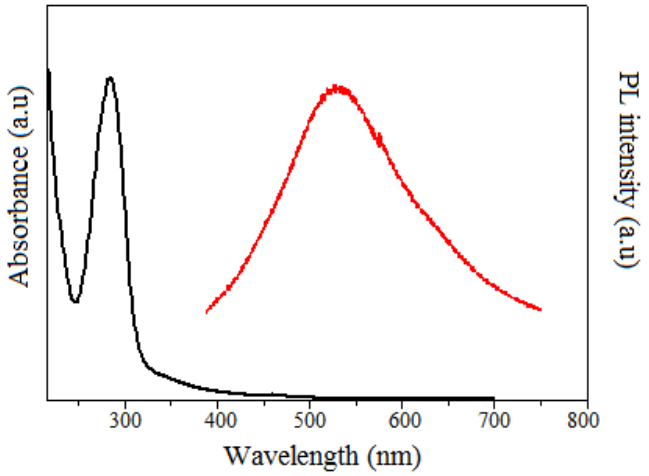

Fig. 4. UV-Vis absorption (black line) and PL (red line) spectra of the Cdots.

The FTIR is applied to explore the surface groups of the Cdots. As revealed in Fig. 5, the absorption bands of O-H stretching vibrations appears at 3440 cm^{-1}. The peaks at 1390 and 2925 cm^{-1}

are assigned to the stretching vibration of C–H [15]. C=O stretching vibrations centered at 1704 cm^{-1} [16].

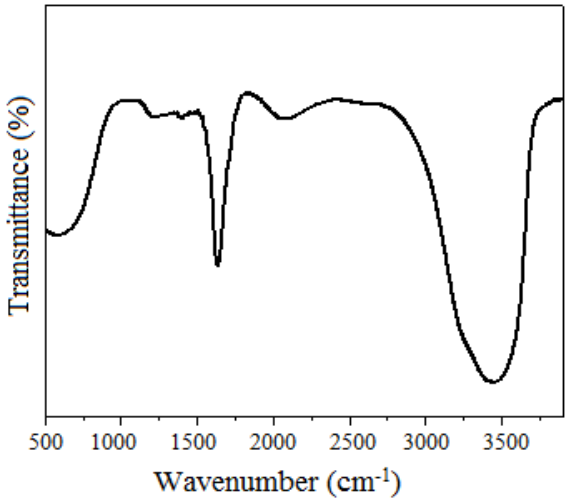

Fig. 5. FTIR spectrum of the Cdots.

As shown in Fig. 6, the selectivity of Cdots to Fe^{3+} was determined by introducing interferent ions (Fe^{2+}, Ca^{2+}, Co^{2+}, Er^{2+}, K^{+}, Mg^{2+}, Mn^{2+}, Na^{+}, Ni^{2+}, Ce^{4+}) under the same conditions. Fe^{3+} had the ability to quench the PL intensity of the Cdots while other metal ions had a little or no quenching effects.

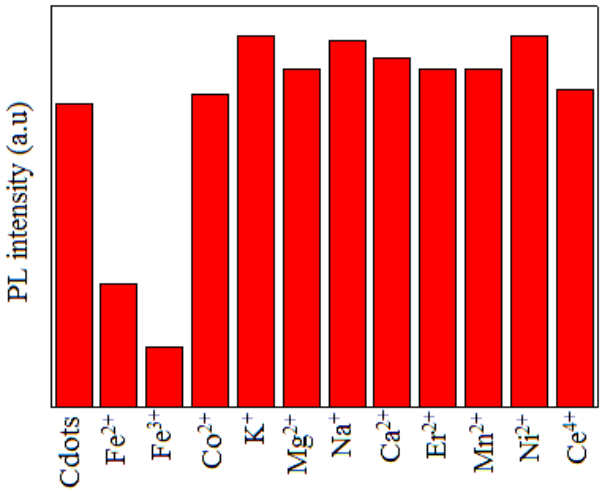

Fig. 6. Effects of metal ions on PL intensity of Cdots.

The selectivity toward Fe^{3+} was also investigated in the presence of other metal ions, as shown in Fig. 7. No obvious PL changing intensity was observed after other metal ions were added. Then, an addition of Fe^{3+} into the above mixtures caused a sharp decrease in PL intensity, which demonstrated that other metal ions showed no interference toward the determination of Fe^{3+} ions.

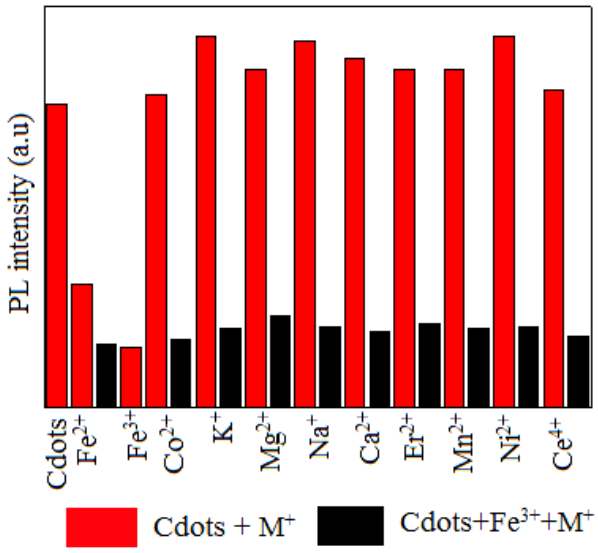

Fig. 7. PL response of the Cdots toward metal ions (red bars) and interference of other metal ions with Fe^{3+} (black bars).

Figure 8 shows PL spectra of Cdots with different Fe^{3+} concentration. The fluorescence intensity of Cdots gradually decreased with the Fe^{3+} concentration. The sensing mechanism for different metal ions could be attributed to energy level alignment between the different PL centers in Cdots and the d state orbits of different metal ions. The combination of surface groups with metal ions through coordinating or chelating interactions bridged the electron transfer (ET) from PL centers to the d state orbits of metal ions. Because the metal-centered d-d states of Fe^{3+} ions were likely situated below the $n–\pi^*$ states of C=O in Cdots, the PL from Cdots was quenched by surface-chelating Fe^{3+} ions via photo-induced ET action [17].

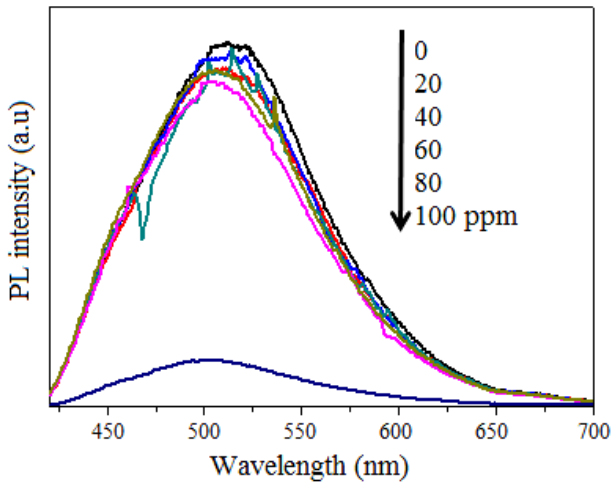

Fig. 8. Influence of Fe^{3+} concentrations on the fluorescence intensity of Cdots (top to bottom: 0; 10; 20; 40; 60; 80; 100 ppm).

As shown in Fig. 9, the fluorescence intensity displayed linear responses with the Fe $^{3+}$ concentration with the linear range of 0 to 80 ppm. The fluorescence quenching efficiency can be further described by the Stern–Volmer plot with a perfect linear behavior with the linear correlation coefficient (R) was ~ 0.93673. The linear equation as: $\frac{F_0 - F}{F} = 0.00154C + 0.01658$ where F_o and F were the fluorescence intensities of Cdots in the absence and presence of Fe $^{3+}$, C is a concentration of Fe $^{3+}$. Limit of detection (LOD) was estimated to be 38.08 ppm based on the equation LOD = 3σ/s where σ is the standard deviation of the blank Cdots and s represents the slope value of calibration plot.

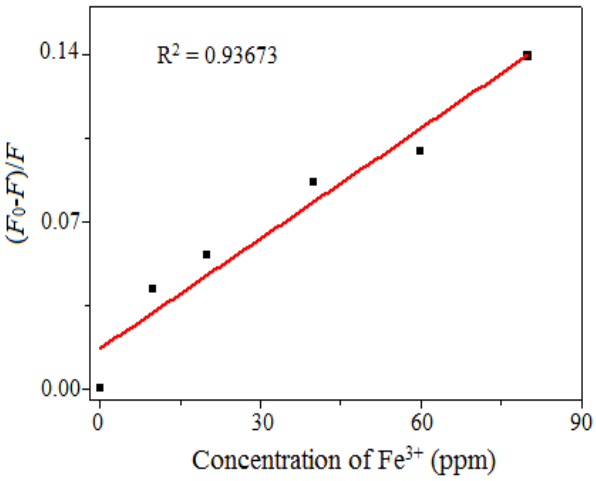

Fig. 9. The linear relation of $(F_o – F)/F_o$ with the concentration of Fe $^{3+}$ in the range of 0 – 80 ppm.

4. Conclusions

Lemon juice has been used as a precursor to produce fluorescent carbon quantum dots via one-step simple hydrothermal method. Additionally, the Cdots exhibit high selectivity and sensitivity and used as fluorescent probes to detect Fe $^{3+}$ with the detection limit of 38.08 ppm.

Acknowledgments

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