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Full Length Article

A facile method to prepare fluorescent carbon dots and their application in selective colorimetric sensing of silver ion through the formation of silver nanoparticles

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ABSTRACT

Herein, we report a laboratory convenient method for the preparation of blue color emitting fluorescent carbon dots (C-dots) in 60 min by boiling the alkaline solution of pectin. The C-dots derived from pectin detects selectively silver ion by forming silver nanoparticles (AgNPs) without any irradiation or heating or additional reducing agents. As prepared AgNPs appears yellow in color and showed the characteristic surface plasmon resonance maximum at 410 nm. Transmission electron microscopy (TEM) revealed crystalline, spherical AgNPs with size range from 10–15 nm. Cyclic voltammetry study revealed that the lower reduction potential of C-dots than that of silver ion favors the reduction of Ag^+ to Ag°. Electrochemical impedance spectroscopy showed the charge transfer value for the redox reaction of C-dots as 200 Ωcm^2. In the presence of Ag^+, C-dots fluorescence emission was turned from blue to cyan to green to colorless, accompanying the quenching and red shift in emission maximum at 450 nm. Interference study clearly showed that the C-dots have high preference for Ag^+ ion than the other interfering metal ions. The proposed sensor system selectively senses Ag^+ ion in water at micromolar concentration and also offers an easy procedure to prepare AgNPs in the presence of other interfering metal ions.

1. Introduction

Carbon dots (C-dots) have recently received significant scientific attention owing to their interesting physicochemical and optoelectronic properties including photostability, photoluminescence and electron transfer behavior [1–3]. The tuneable photoluminescence properties have found useful *in vitro* and *in vivo* bioimaging [4–6]. The electron donor and electron acceptor potential of C-dots have found successful in sensing and photocatalytic application [7–10]. Moreover, C-dots are biocompatible and less toxic than the traditional semiconductor quantum dots [11,12]. Therefore, from the time of discovery by Xu et al., several new applications are emerging for C-dots [13]. This leads to the development of several synthetic techniques including laser ablation, electrochemical synthesis, arc discharge, hydrothermal and microwave heating, etc [14–17]. Most of these methods are either required complex post-treatment or required sophisticated instrumentation. There are very few reports exist on the synthesis of C-dots by simple techniques, such as dehydration of carbohydrates by strong acids, alkaline treatment of cetylpyridinium chloride monohydrate and oxidation of capsicum extract [18–23]. Of late, there is considerable progress in the synthesis of C-dots through green chemistry method utilizing natural bio-resource, such as orange peel [17], soya milk [24], cow milk [25] and apple juice [26]. Despite the advantages, the use of renewable bio-precursors suffers from the uncertainty about the chemical components responsible for the formation of C-dots. Therefore, a more defined, more robust, cost-effective and eco-friendly approach is still warranted for large scale preparation.

Pectin is a natural carbohydrate polymer present in the pomace of citrus fruits. It is composed of a linear backbone of (1-4) linked α-D-galacturonic acid residue with varying degree of methylesterified carboxyl groups. It is widely used as gelling, thickening and stabilizing agent in the food industry [27,28]. In this paper, we described a laboratory convenient method to synthesize blue fluorescence C-dots by simply heating the alkaline solution of pectin in a round bottom flask. The proposed method to obtain blue color emitting C-dots is quite different from other protocols where the formation of pectin hydrogel and hydrothermal treatment is a prerequisite for the preparation of C-dots [29]. The formation of C-dots and their fluorescent behaviour under various conditions were investigated. A possible mechanism for the formation of the C-dots from pectin was proposed from the collective information obtained from the

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literature reports on the carbonization of carbohydrates [30–34] and also by the help of FTIR and ^{1}H NMR analysis.

Of late there has been great interest in exploiting the fluorescence C-dots for selective and sensitive detection of heavy metal ion, sulfide ion, glutathione, tetracyclines [35–40]. Herein, we report that the C-dots derived from pectin detect silver ion through the formation of yellow color silver nanoparticles (AgNPs). As prepared AgNPs was characterized by UV–visible, TEM and zeta potential analyzer. For the first time, the reduction potential of C-dots was estimated by cyclic voltammetry. The estimated negative reduction potential of C-dots than that of silver ion favours the sensing through electron transfer reaction. Moreover, the proposed sensing system offers an eco-friendly method to obtain stable AgNPs without any reducing agent or irradiation or heating.

2. Materials and methods

2.1. Materials

Sodium borohydride and sodium hydroxide were purchased from Merck, India. Silver nitrate was purchased from Fisher Scientific, India. Pectin was obtained from Alfa Aesar. All the glassware were cleaned with freshly prepared aqua regia (3:1, HCl: HNO_3) and rinsed thoroughly with water. Then they were dry sterilized using hot air oven at 160 °C for 3 h, prior to use.

2.2. Preparation of carbon dots

For the preparation of C-dots, pectin from citrus peel (Alfa Aesar, India) was used and characterized by ^{1}H-NMR (Burker 300 MHz) and the pectin degree of esterification was determined by the titration method (see supporting information). Typically, alkaline pectin solution was prepared by dissolving 100 mg pectin in 10 mL of 100 mM NaOH solution and stirred for about 30 min and then brought down to room temperature. This mixture is transferred carefully to a round bottom flask and heated in the laboratory heating mantle for 60 min. The appearance of the dark brown color indicates the formation of C-dots. The formation of fluorescent C-dots was confirmed by observing blue color fluorescent while irradiating at 360 nm using UV–vis lamp. The excess unreacted NaOH was removed by dialysis (dialysis bag cut off 1000 Da) against double distilled water for 24 h.

C-dots fluorescence spectra were recorded on a Jasco-FP8200 spectrofluorimeter. The spectral slit width was set at 2.5 nm for both excitation and emission monochromators. UV–vis absorption spectroscopy was performed on Thermo Scientific Evolution 201 spectrophotometer operated at 1 nm resolution. The size and morphology were examined using transmission electron microscopy (TEM) (JEOL-JEM 1011, Japan) operating at an accelerated voltage of 200 kV. The samples were prepared by placing a drop of NP solution on a graphite grid and drying it in vacuum. The dried powders of C-dots were subjected to FTIR spectroscopy measurements. These measurements were carried out on a Perkin-Elmer spectrum-one instrument in the diffuse reflectance mode at a resolution of 1 cm^{-1} in KBr pellet. ^{1}H NMR was measured in a Bruker 300 MHz instrument.

2.3. Sensor studies

C-dots prepared with 100 mM NaOH was used for the sensor studies. Metal ion for sensor studies was prepared by mixing the requisite amount of salt in double distilled water. Typically, 200 μL of C-dots was added to 9.8 mL of water containing different metal ions and monitored the color change. The assays and the changes in absorption and fluorescence spectra were performed and monitored at room temperature. The photographs were taken with a digital camera after 10 min of mixing.

2.4. Electrochemical studies

All electrochemical studies were carried out in aqueous medium using a platinum disc working electrode, platinum wire counter electrode and saturated calomel electrode as reference electrode (CHI660E electrochemical workstation; CH Instruments, USA). Electrochemical impedance studies were carried out over a frequency range of 1 Hz to 1 MHz with an ac amplitude of 5 mV and the data were fitted with modified Randle's circuit for a diffusion controlled process (R(C(RW)) using ZSimpWin software (EG & G).

3. Results and discussion

The preparation of C-dots using biopolymer, pectin was illustrated in Fig. 1A. Initial experiments were carried at room temperature by mixing 10 mL of aqueous suspension of pectin (100 mg) with 100 mM of NaOH. The color changes from colorless to light yellow indicating the carbonization of pectin. It has been noted that the color change is accompanied by the formation of precipitates in the bottom of the test tube. These solutions produced greenish blue fluorescence under UV irradiation (Fig. 1). Considering the non-fluorescent nature of the starting material, the obtained fluorescence can be attributed to the presence of C-dots in the solution. Attempts were also made to synthesis C-dots at room temperature with varying concentration of NaOH. Every time, the C-dots preparations end up with the formation of precipitates at the bottom, moreover, these solutions showed very weak fluorescence (Fig. S1A and C).

To obtain highly fluorescent C-dots, we boiled (100 °C) the alkaline solution of pectin in a laboratory heating mantle. Heating the alkaline pectin solution in a laboratory heating mantle proceed with a color change from light yellow to brownish yellow in 60 min, indicating complete carbonization (Fig. 1 and Fig. S1B). As-prepared C-dots showed strong blue fluorescent under UV

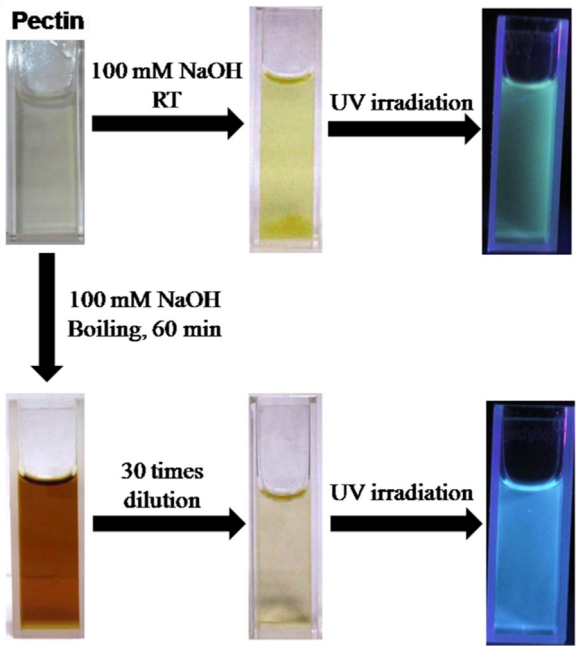

Fig. 1. Schematic preparation of C-dots from pectin.