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Carbon dots production via pyrolysis of sago waste as potential probe for metal ions sensing

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ABSTRACT

This work reports the synthesis of carbon dots (C-dots) from sago industrial waste using thermal pyrolysis approach. The pyrolysis condition was found to govern the carbonisation conversion of bulk sago waste into carbon rich residue that can be further isolated to obtain carbon dots. In order to obtain the best yield of the carbon dots, optimization of the thermal pyrolysis conditions have been performed which consisted of varying temperature of carbonisation at a constant heating duration. The C-dots can be dispersed in aqueous media and portrayed a significant fluorescent property that can be observed by naked eye under a UV light source. The optimum temperature of carbonisation was determined at 400 °C in which the strongest fluorescence emission was record at 390 nm with the optimum excitation wavelength of 315 nm. The fluorescence of the C-dots was found to be significantly quenched in the presence of various metal ions. Thus, the C-dots can be adopted as a potential optical probe for sensing of metal ions in aqueous media. An analytical characterization has been performed in this study over a series of commonly available metal ions and the sensing characteristics were evaluated using the standard Stern–Volmer quenching model. This study has successfully demonstrated an innovative approach of converting agricultural waste into high value optical sensing receptors for metal ions detection.

1. Introduction

In the recent years, fluorescent carbon nanoparticles or carbon dots (C-dots) have drawn considerable interest due to their stable photoluminescence property, and broad ranges of excitation and emission spectra. They have 'almost-spherical' shapes and are synthesizable via relatively simple methods from various starting precursors [1]. Ideally, C-dots were reported to have stable photoluminescence (PL) properties, great biocompatibility, and low cytotoxicity effects towards biological components as compared to their counterparts, the semiconductor quantum dots (Q-dots) [2,3]. Q-dots are generally toxic and have been known of affecting health and environmental conditions as it comprised of elements from the periodic groups II–VI, III–V or IV–VI [3,4]. C-dots have since then known to be important and stand to have huge impact along with their promising applications and preliminary outcomes in various fields [5].

The synthetic routes of these non-toxic fluorescing C-dots include arc-discharge, acid dehydration, electrochemical oxidation, laser ablation, hydrothermal reaction, and combustion (thermal) supported methods, which in general can be categorized into: (i) top-down and (ii) bottom-up methods [1,4,6]. Majority of the synthesis methods require complicated equipments, catalysts, non-environmental friendly chemicals or harsh experimental conditions which results in expensive production costs. Thus, there is on-going focus on the development of simple and economical methods to synthesize C-dots [2]. Among those, combustion (thermal) supported methods, otherwise, known as pyrolysis of carbonaceous materials is a simple, clean and inexpensive synthetic option [7–10]. Thermal degradation synthesis routes have shown to be successful via microwave- and furnace- assisted pyrolysis as demonstrated by Yang et al. [11], Liu et al. [3], and Wang et al. [12]. Pyrolysis parameters such as type of reactor system, heating temperature, pressure, presence of catalysts, and heating duration are found to affect the composition and yield of the end-products depending on [9].

There are varieties of carbon-rich starting precursors that can be used to synthesize C-dots. Along with the uprising global awareness of creating a sustainable community via waste minimization, the choice of recycling and reusing carbon-rich waste as starting

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materials for synthesis of C-dots will be of advantage. Besides, wastes are inexpensive and renewable resources, whereas some biomass wastes have been demonstrated as suitable starting precursors for the synthesis of C-dots [13–15].

In addition to the effort of searching for alternative synthesis routes and precursors, there is also an increase of interest that focuses on the practical application of C-dots. The applications of C-dots as fluorescence probe for optical sensing of metal ions have been studied by several researchers and the outcomes of their studies were promising. The C-dots were able to selectively and sensitively detect metal ions in aqueous solution [3,16,17]. The presence of toxic heavy metal ions in the environment, particularly in aquatic systems remains as one of the major environmental concerns to-date [18]. Highly selective and sensitive analytical methods such as atomic absorption spectroscopy [19,20], liquid chromatography [21–23], adsorptive stripping voltammetry [24], electrochemical analysis [25] and spectrophotometric analysis [26] have been used to qualify and quantify the levels of metal ions in the environment. Yet, these analytical methods require high operating cost, use of hazardous chemicals and involvement of tedious preparation procedures. Hence, it is not feasible and sustainable in long-term and there is a need to develop alternative analytical methods that are more economical, selective, sensitive, remains user-friendly and green to the environment. Fluorescence quenching has shown to be one of the promising alternative approaches for metal ions detection [27]. Previously, Q-dots based fluorescent probes derived from silicon, and heavy metals such as lead and cadmium have been evaluated for optical sensing application [28]. Nonetheless, the toxicity effect and possible leaching of heavy metals from Q-dots remains a challenge that significantly limits their practical applications. Alternatively, C-dots that exhibit equivalent fluorescence characteristics as Q-dots yet possessing lower toxicity and production cost may serve as potential fluorescing nanomaterial for optical sensing of metal ions.

In search for a simple alternative synthesis route of C-dots from low cost starting material, the sago waste from the industry has been chosen in this study. Particularly in East Malaysia, the sago starch industry is one of the major food industries producing approximately 260 tonnes of sago wastes consisting of woody bark, wastewater and fibrous sago pith. These wastes are usually disposed to the nearby streams and consequently resulting in an increase of pollution load [29]. Hence, this study will demonstrate the conversion of sago industrial waste into fluorescing C-dots, a biotechnological approach to recycle and reuse the sago industrial waste. The synthesis method involved the pyrolysis of sago industrial waste in a laboratory furnace which is simple and economical. Heating temperatures between 250 °C and 450 °C were investigated to carbonize the sago industrial waste into carbon residues. Experimental parameters, particularly the heating temperature relating to the pyrolysis of starting materials were evaluated to obtain C-dots with optimum optical property. The optical sensing potential of the C-dots for metal ions has been studied and its analytical characteristics were evaluated and discussed.

2. Experimental

2.1. Materials and reagents

Sago industrial waste as starting precursor was obtained from local sago industry (Bau, Kuching, Sarawak, Malaysia). The waste was pre-dried in a drying oven for a week at 40 °C and was later ground into powder with a grinder. All chemicals involved in the study were of reagent grade and used without further purification. Metal salts of $Cu(NO_3)_2$, $Cr(NO_3)_2$, $Co(NO_3)_2$, $Ni(NO_3)_2$, $Al(NO_3)_3$, $Ca(NO_3)_2$, $Pb(NO_3)_2$, $Zn(NO_3)_2$, $SnCl_2$ and $HgCl_2$ were all purchased from R&M Marketing (Malaysia). Ultrapure water obtained from MiliporeMili-Q Advantage-A10 and Millipore Elix-5 water purification system (~18.2 Ω, 25 °C) was used as solvent system throughout the experimental work.

2.2. C-dots synthesis

C-dots were prepared via pyrolysis method as illustrated in Fig. 1. In brief, appropriate mass of pre-dried and ground sago waste was weighed into a crucible and transferred into a laboratory furnace (Carbolite ELF 11/14 B). The sample was heated from room temperature to a final temperature (ranging from 250 °C to 450 °C), with no gas flow and kept at the set temperature for 1 h. After the heating process, the resulting product was allowed to cool to room temperature in a desiccator before a mixture with a mass concentration of 10 g/L was prepared. Briefly, an exact amount of 0.0100 g of heat treated sago waste was weighed into a volumetric flask and dispersed with 10 mL of ultrapure water. The mixture was then homogenized under sonication (Branson 5510 Ultrasonic cleaner) for 2 h and was later subjected to centrifugation (EppendorfMinispin) at 13,400 rpm for 20 min to remove the bulk particles. The supernatant was finally collected and diluted to a ratio of 1:2 for optical analysis.

2.3. Instrumentation

Fluorescence measurements were recorded using fluorescence spectrophotometer (Varian Cary Eclipse Fluorescence Spectrophotometer). The isolated C-dots were diluted with ultrapure water to an appropriate concentration and then transferred into a quartz cuvette of four clear windows with a path length of 1 cm. The settings of excitation and emission wavelengths were adjusted accordingly for C-dots samples treated at different conditions to obtain its respective highest emission intensity. The excitation and emission slits of the fluorescence spectrophotometer were both set at 5 nm for all measurements. UV absorbance of samples was determined via UV–visible spectrophotometer (Varian Cary 50 Conc UV-Visible Spectrophotometer). Similar concentrations of C-dots as prepared for the fluorescence analysis were used and measurements were made in a quartz cuvette with two clear windows and a path length of 1 cm. The absorbance of samples was monitored between 200 nm and 800 nm. Ultrapure water was used as reagent blank for both instruments. Scanning Electron Microscope (SEM) (JEOL JSM-6930 LA) operated at zeta potential of 10 kV was used to characterize the physical properties of synthesized C-dots. Sample for SEM analysis was prepared by dispensing 10 μL of supernatant containing C-dots onto a 1 cm × 1 cm platinum plate. The plate was placed in a dessicator overnight to concentrate C-dots by removing water. SEM images of samples were analyzed via SmileView (JEOL version 2.2) for estimation of particle sizes. Fourier Transformed Infrared (FTIR) (Perkin-Elmer) was used to characterize the organic functional groups on C-dots. The supernatant containing C-dots was concentrated by removing water under vacuum, in a freeze dryer (LABCONCO FreezeZone 6 Freeze Dryer). The resulting solid residue was then used for the analysis.

2.4. Optimization of pyrolysis variables

The effects of temperature of the furnace on the photoluminescence of C-dots derived from sago waste were investigated. In this work, the intensity of the fluorescence of the isolated product was used as a measure on the production efficiency of the C-dots. It is derived that higher intensity recorded denotes larger amount of C-dots produced. A series of end-heating temperatures were fixed from 250 °C to 450 °C at an interval of 50 °C and each of the heating process was left to stand for an hour. Besides evaluating the