



Green synthesis of carbon dots from prawn shells for highly selective and sensitive detection of copper ions



Gangaraju Gedda^d, Chun-Yi Lee^a, Yu-Chih Lin^a, Hui-fen Wu^{a,b,c,d,e,*}

^a Department of Chemistry, National Sun Yat-Sen University, 70, Lien-Hai Road, Kaohsiung 80424, Taiwan

^b School of Pharmacy, College of Pharmacy, Kaohsiung Medical University, Kaohsiung 807, Taiwan

^c Institute of Medical Science and Technology, National Sun Yat-Sen University, 70, Lien-Hai Road, Kaohsiung 80424, Taiwan

^d Doctoral Degree Program in Marine Biotechnology, National Sun Yat-Sen University and Academia Sinica, Kaohsiung 80424, Taiwan

^e Center for Nanoscience and Nanotechnology, National Sun Yat-Sen University, 70, Lien-Hai Road, Kaohsiung 80424, Taiwan

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ABSTRACT

A facile, economical and effective green method was developed for synthesis of fluorescent carbon dots (C-dots) from prawn shells. The results showed that these C-dots (with an average diameter of 4 nm) possess many excellent features such as to eliminate blue fluorescence under UV light ($\lambda = 365$ nm), with high monodispersity, good stability, excellent water solubility and high quantum yield (9%). We further explored these C-dots as effective sensing probes for Cu^{2+} detection and found that they exhibit excellent selectivity and sensitivity toward Cu^{2+} with a low detection limit of 5 nM. We further demonstrated this novel sensing platform on Cu^{2+} ions analysis from seawater samples. This method is extremely rapid, low cost, ecofriendly, highly selective and sensitive for Cu^{2+} ions sensing from various sources of environment such as drinking water, river water and sea water.

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1. Introduction

Marine crustacean wastes such as squilla, krill, prawn, crab and lobster shells are industrial by-products. The worldwide seafood industries are estimated to generate approximately 60,000–80,000 tons of crustacean waste in one year [1]. The discarding of such large quantity of crustacean waste is a serious environmental problem especially because of they are resist to biodegradation, insoluble in water and to process the waste is a high cost [2,3]. The crustacean waste contains a large quantity of chitin (about 20–30% of body weight depending on the organisms) and small quantity of proteins, minerals (mainly calcium), lipids and pigments [4]. The chitin and its deacetylated derived components (including chitosan) have been widely used for various environmental purposes such as water treatment, paper production, anti oxidant, antibacterial and antifungal reagents. Moreover, chitosan has been widely used for detecting many heavy metals such as Cu^{2+} , As^{2+} , Hg^{2+} , Cd^{2+} , etc. due to their excellent chelating ability with heavy metals [5,6]. Therefore, the proper usage of the crustacean waste is not only to solve the disposal problems but also to serve as a new

platform for many fields including industry, biomedicine, food processing, cosmetics and agriculture [7]. For sensible utilization of the marine crustacean waste, we developed carbon dots based sensors for sensing the copper(II) ions.

In recent decades, considerable efforts have been devoted to developing various analytical methods for sensing chemically and biologically important drugs, biomolecules, metal ions especially focused on the detection of toxic metal ions and organic pollutants [8–30]. Among these applications, the monitoring on copper ions has received increasing attention in toxicological point of view. It is often present in natural and environmental water such as seawater, river/lake water, drinking water and tap water [31,32]. Copper is an essential transition metal for human beings and also plays a crucial role in biological systems. However, it is severely toxic at higher concentrations with long-term of exposure with the human body. It can cause many neurodegenerative diseases such as Wilson's, Prion and Alzheimer diseases [33,34]. According to the U.S Environmental Protection agency, the upper limit of copper ions in drinking water is 20 μM [35]. Therefore, it has extremely highly demand to monitor copper concentrations with high sensitivity and selectivity from the environment. Although, currently various analytical techniques are available for detecting copper including potentiometric sensors, electrochemical sensors, atomic fluorescence spectrometry, atomic absorption spectrometry (AAS) and inductively coupled plasma mass spectrometry (ICP-MS) [15,36–41]. They may detect

* Corresponding author at: Department of Chemistry, National Sun Yat-Sen University, 70, Lien-Hai Road, Kaohsiung 80424, Taiwan.

E-mail address: hwwu@faculty.nsysu.edu.tw (H.-f. Wu).

copper with high sensitivity, but their applications are limited due to high cost, time-consuming, complicated sample preparation and inappropriate for real-time monitoring. As to the fluorescence assay methods have been used for sensing many metals with many advantages like high sensitivity, selectivity, simple sample preparation, rapidity and less interferences [42,43]. In recent years, many reports reveal that the fluorescent materials including semiconductor quantum dots and organic dyes have been used for sensing metals [43–46]. However, these methods are limited with the following features. (1) Multiple synthesis and purification steps are required. (2) The nanomaterials are prepared from highly toxic and expensive chemicals such as precursors and surface modifiers. Thus, it is great demand to develop a new, a facile, rapid, inexpensive and green method for the production of biocompatible fluorescent nanomaterials.

Xu et al. [47] accidentally found carbon dots (C-dots) during the purification of single-walled carbon nanotubes by electrophoresis in 2004. C-dots gained considerable attention due to their unique physical, chemical, optical and photoluminescence properties [48]. Compared to the conventional semiconductor quantum dots and organic dyes, the fluorescent C-dots are superior in many aspects especially in simple and rapid synthesis process, excellent water solubility, high biocompatibility, less toxicity and high photostability. Because of these outstanding properties, they can be used to replace the toxic quantum dots in many clinical and environmental applications [49,50]. So far, a variety of synthesis methods toward C-dots have been developed such as laser ablation, arc discharge, electrochemical oxidation, microwave and hydrothermal [51–54]. However, they are not ideal choices, because most of these approaches suffer from some disadvantages like the use of a high quantity of strong acids, low quantum yield and involvement of complex process. Moreover, additional expensive surface passivating agents were used to enhance their fluorescence property and selective sensing of metals [55]. From the environment, material synthesis and sensing point of views, the study of new carbon source for facile, economical, simple and green synthesis of such C-dots from waste materials without additional surface passive agent is highly desired.

Here, we demonstrate the use of cost-free seafood waste as the new carbon source for the green synthesis of water-soluble fluorescent C-dots without using any surface passive agent. This method can recycle the environmental wastes for the preparation of C-dots. We further demonstrated that seafood waste derived C-dots can serve as label-free fluorescent sensors for selective and sensitive detection of Cu^{2+} . To demonstrate the practical application of this fluorescence sensing system, it is further applied to monitor Cu^{2+} ions from seawater.

2. Materials and methods

2.1. Chemicals

Disodium hydrogen phosphate (Na_2HPO_4), sodium di-hydrogen phosphate (NaH_2PO_4), Potassium dihydrogen phosphate (KH_2PO_4), Hydrogen chloride (HCl), Sodium hydroxide (NaOH), MgSO_4 and Glacial acetic acid were purchased from Sigma. AgNO_3 , CdCl_2 , $\text{Mg}(\text{OAc})_2$, NiCl_2 , FeCl_2 , $\text{Hg}(\text{NO}_3)_2$, $\text{Pb}(\text{NO}_3)_2$, and ZnCl_2 obtained from Alfa aesar. Na_2SO_4 , NaCl, KCl, CaCl_2 , CuCl_2 , MnCl_2 obtained from Merck. CoCl_2 was obtained from J.T. baker. All aqueous solutions were prepared using ultrapure deionized water from a Milli-Q purification system (Millipore, Milford, MA, USA).

2.2. Instrumentation

TEM images of C-dots were recorded by using transmission electron microscopy (TEM-3010, JEOL, Japan). The UV–visible spectrum

of C-dots was recorded by using double beam UV–visible spectrophotometer (Hitachi U-3501, Japan). The fluorescence emission spectra of C-dots were recorded by using a fluorescence spectrophotometer (Hitachi, F-2700, and Japan). The elemental composition of C-dot was observed by energy-dispersive X-ray spectroscopy (EDXS, Oxford Instruments, UK). X-ray diffraction (XRD) patterns were obtained by XRD spectroscopy (Bruker D8 Advance, Germany). C-dots functional groups investigated by Fourier transform infrared spectrometer (Bruker FT-IR IFS-48, Germany).

2.3. Sample collection and pretreatment

Prawn shells were bought from Kaohsiung local market, Taiwan. The prawn shell was washed with tap water and followed by deionized water. The cleaned samples were dried overnight at 80°C . The dried shells were ground by mortar and pestle to make the fine powder. Seawater was collected from Shizwan Bay, Kaohsiung, Taiwan. The seawater samples were filtered through the $0.22\ \mu\text{m}$ membranes (Millipore, USA) prior to the detection.

2.4. Synthesis of C-dots

2.0 g of dried prawn shell powder was treated with 25 mL of 3% NaOH solution at room temperature for 5 h. The powder washed with deionized water until a neutral pH was obtained. The sample was treated with 1% hydrochloric acid solution for 6 h at room temperature. After acid treatment, the sample was washed with deionized water by several times to obtain a neutral pH. The prawn shells were transferred to a 50% sodium hydroxide solution and refluxed at 80°C for 2 h. The refluxed sample was cooled down to the room temperature and filtered through with (Whatman) filter paper. The obtained product was dispersed in 25 mL of 2% acetic acid solution. Then the sample was transferred to 45 mL capacity stainless steel autoclave and kept at 200°C for 8 h. The C-dots were collected by removing the large particles through centrifugation at 14,000 rpm for 20 min and finally dried under vacuum for overnight. The C-dots were dispersed in deionized water at a concentration of $1\ \text{mg mL}^{-1}$ for further characterization and use.

2.5. Quantum yield measurement

The quantum yield (Φ) of C-dots was estimated by comparing the integrated PL intensities and the absorbency values against the reference quinine sulfate. Quinine sulfate (from literature $\Phi = 0.54$) was dissolved in 0.1 M H_2SO_4 (refractive index (η): 1.33), and the C-dots were dissolved in deionized water (η : 1.33).

$$\Phi = \Phi_r \left(\frac{I}{I_r} \right) \left(\frac{A_r}{A} \right) \left(\frac{\eta^2}{\eta_r^2} \right)$$

Here Φ is the quantum yield, I is the measured integrated emission intensity, η is the refractive index, and A is the optical density. The subscript r represents the reference fluorophore of known quantum yield.

2.6. Fluorescence assay of Cu^{2+}

The sensing of Cu^{2+} was performed at room temperature in PBS (0.2 M, pH 4.0) solution. In a typical experiment, the desired amount of Cu^{2+} (final concentration 0–5 μM) ions was added to 1 mL of PBS solution containing C-dot (final concentration 20 $\mu\text{g/mL}$). The fluorescence emission spectra were recorded after reaction for 15 min at room temperature. The reaction time, pH effect, sensitivity and selectivity measurements were conducted in triplicate measurements for all experiments.

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