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RESEARCH PAPER

Synthesis of carbon nanoparticles from waste rice husk used for the optical sensing of metal ions

Peggy Zhen Zhen Ngu[1], Stephanie Pei Phing Chia[1], Jessica Fung Yee Fong[1,2], Sing Muk Ng[1,2*]

[1]Faculty of Engineering, Computing, and Science, Swinburne University of Technology Sarawak Campus, Jalan Simpang Tiga, 93350, Kuching, Sarawak, Malaysia;

[2]Swinburne Sarawak Research Centre for Sustainable Technologies, Swinburne University of Technology Sarawak Campus, Jalan Simpang Tiga, 93350, Kuching, Sarawak, Malaysia

Abstract: This work reports on a synthesis of carbon nanoparticles (CNPs) from waste rice husk by thermally-assisted carbonization in the presence of concentrated sulfuric acid. The fluorescent emmision characteristics of the CNPs, their quenching effects by metal ions and their use as a sensing material for Sn(II) ions were investigated. Results indicated that the yield of CNPs was optimized at a sulphuric acid concentration of 12 mol/L, heating temperature of 120 °C and heating time of 30 min. The sample showed a strong blue luminescence in water with a maximum emission at 439 nm. The fluorescence can be quenched by adding various metal ions by the formation of complexes between the metal ions and surface of the CNPs. Sn(II) ions had the most significant quenching effect on the fluorescence of the CNPs, which is concentration-dependent. The concentration dependent quenching was linearized with the Stern-Volmer equation, and showed a linear response up to a Sn(II) concentration of 6.13 mmol/L. The limit of detection for Sn(II) ions is 18.7 μmol/L with good repeatability.

Key Words: Carbon nanoparticles; Fluorescence; Quenching; Sensing; Metalions

1 Introduction

Nanomaterials are of great scientific interest owing to their small dimension and unique physical properties that are different from the bulk materials. Bulk materials often show constant physical properties while nanomaterials have the size-dependent properties such as the quantum confinement effect that gives rise to the fluorescence property for some semiconductor nanoparticles [1]. The colour of the emission can be tuned by changing the average size of the nanoparticles [2]. Besides, the large surface area due to the small size has enhanced affinity toward the solvent molecules. This phenomenon allows the formation of a colloidal solution since the nanomaterials can be dispersed homogenously within the solvent and interface interactions between the nanomaterials and others existing species within the solvent occur under this condition. Hence, with a synthesized of these unique physical and colloidal properties, the nanomaterials can be used for several applications such as sensing [3], drug delivery [4] and environmental remediation [5, 6].

Various nanomaterials have been synthesized and the effort to produce new novel nanomaterials is still on-going. The main motivation is to incorporate better physical properties and chemical functionalities into the nanomaterials to improve its performance in applications. In addition, there is also a need to search for new nanomaterials that are more sustainable, which not only non-toxic, biocompatible and environmental friendly, but also the synthesis adopting green production methods and using renewable precursors. Carbon nanoparticles (CNPs) are the latest alternative of nanomaterials that have been discovered and portrayed several advantages over other existing nanoparticles. Similar to the well-known quantum dots, CNPs show bright fluorescence, high photostability, and tuneable excitation and emission spectra [7, 8]. In addition, CNPs are less-toxic, soluble in water and have good biocompatibility, non-blinking fluorescence, chemical inertness[9]. Their low molecular weights as well as small sizes make them a good candidate for drugs delivery [10, 11]. The work by Baker [12] has reported on the potential of CNPs to be used for bio-imaging, drug delivery and diagnostic tools. In a separate study, Yang et al. [13] has demonstrated that CNPs showed no or low toxicity when tested *in vivo* on mice, hence had less concern on the safety issue even for some applications within the human body.

In the early stage of CNP development, the synthesis methodologies taken are based on the top-down approach. It requires the formation of CNPs from bulk carbon sources such as bulk graphite via various harsh mechanical processes. One of the examples is through the use of laser ablation to produce the nano-sized carbon particles, where strong laser beam is focused onto a carbon target, eventually causing the formation of arc-discharge soots. The soots upon surface passivation using oxidizing agents often showed good fluorescence and water soluble properties. In fact, this method has been

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***Corresponding author.** E-mail: smng@swinburne.edu.my

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employed in the work by Xu et al. [14], which is believed to be the first work reported on the isolation of fluorescent CNPs. Although the top-down approach produces purer CNPs, the instrumental setup to perform the mechanical cracking of carbon is often sophisticated and expensive. Small scale laboratories without high technological facilities installed and sufficient financial funding supports will not be able to produce CNPs through this route. Therefore, continuous effort in search for alternatives has led to the more sustainable bottom-up approach, where CNPs are formed from simple molecular precursors via chemical process. This approach utilizes precursors that are often readily available and cheap in cost. Besides, the methods adopted for the bottom-up synthesis are also much easier with fewer steps, more basic laboratory setups and lower energy consumption than the top-down ones. Liu et al. [15] reported a facile synthesis of CNPs using candle soots, while Sahu et al. [16] demonstrated the production of CNPs from the carbonization of orange juice.

Herein, we propose and demonstrate a simple yet novel method to synthesis CNPs from waste rice husks based on a thermal-assisted acid carbonization approach using sulfuric acid. The proposed method focuses on the aspect of sustainability by adopting green chemistry for synthesis, using safe and renewable resource as starting precursor. Rice husk is a good candidate as starting precursor since it is considered as agricultural waste, renewable resource, considerably cheap, and can be obtained easily in bulk. Majority of rice-producing countries burn the rice husks in open piles that can cause serious air pollution. Others dump them at open landfills, where these rice husks are left to rot and eventually can lead to the production of methane, a greenhouse gas that causes global warming [17].

The colloidal interactions of the CNPs with some metal ions have been investigated with the attempt to utilize such interfacial phenomena for a real application. The synthesis method suggested in this study is novel and sustainable, but the effort will be underutilized if the CNPs have no further usage. Metal ions were selected in the study owing to their positively charged nature that poses a high probability to interact with the surface of the CNPs, as the surface is rich with carboxyl groups after the acid carbonization process. The effect of the intersurfacial interactions of CNPs with metal ions on the fluorescence emission was monitored and characterized towards optical sensing application. Particularly in this study, the fluorescence of the CNPs was characterised towards the detection of stannous ions (Sn(II) ions).This work suggests an option to convert cheap agricultural waste into advanced optical sensing nanomaterial of high commodity value. In addition, the CNPs can act as an alternative to replace the use of some existing fluorescent dyes or quantum dots that are produced from far less sustainable approaches as compared with the CNPs reported in this work.

2 Experimental

2.1 Chemicals and reagents

All chemicals involved in this study were of analytical grade and used as received without further purification unless otherwise stated. Ultrapure water (~18.2 MΩ, 25 ºC) was obtained from a Milipore Mili Q-system and used as solvent throughout the study. Rice grains were obtained from a local rice-hulling mill (Sibu, Sarawak) and the husk was carefully peeled off from the rice grain. The rice husks were washed for 3 times and soaked in water for at least 12 h, before rinsed with water and dried in oven for 30 min before use. Concentrated sulphuric acid (H_2SO_4, with a concentration of approximately 18 mol/L) was used as dehydrating agent for the carbonization. For the intersurfacial interaction study with metal ions, heavy metal ions stock solutions were prepared in deionized water from the respective salts of ($Cu(NO_3)_2$, $SnCl_2$, $Ni(NO_3)_2$, $Al(NO_3)_3$, $Co(NO_3)_2$, $Pb(NO_3)_2$, $AgNO_3$ and $HgCl_2$) that were all purchased from R&M Marketing, Malaysia.

2.2 Instrumentation

Fluorescence intensity was recorded using a standard lab based spectrofluorometer (CARY Eclipse, Varian) set under the fluorescence mode. To do the measurement, the sample was transferred in a quartz cuvette with a path length of 10 mm and four-side windows cleared and polished . The cuvette was placed in the spectrofluorometer and the emission was recorded with the slits set at 5.0 and 10.0 nm for the excitation and emission paths, respectively. The pH was adjusted using acid and base and the value was monitored with a pH meter (Mettler Toledo SevenEasy). Carbonization temperature was controlled using a standard laboratory furnace (Carbolite ELF 11/14B). The separation for nanoparticles was performed by centrifugation method using a centrifuge system (Eppendorf Minispin).

2.3 Synthesis of CNPs

The bottom-up approach was employed to synthesize the CNPs via simple carbonization of rice husks using H_2SO_4. In this study, high temperatures were adopted to assist and speed-up the carbonization. In brief, 0.200 g of cleaned and dried rice husks were transferred into a small beaker, to which 2.0 mL of H_2SO_4 (12 mol/L) was added. The beaker was then wrapped using an aluminium foil and heated in an oven at 120 $^{\circ}$C for 30 min under air, which resulted in the formation of black residue at the end of the heating. The residue was divided approximately into two portions and each transferred into a 2.0 mL microcentrifuge tube. The beaker was rinsed using 2.0 mL of ultrapure water and likewise divided into two portions and transferred into the same two tubes containing the initial residue. The tubes were centrifuged at 13,400 r/min for 15 min. The supernatant of yellowish-brown in colour was then collected using Millipore syringe filters (size of 0.1 mol/L) and redispersed into ultrapure water. Strong blue luminescence was observed upon irradiation of the redispersed solution under an UV transilluminator. The sample solution