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Synthesis of carbon nanoparticles using one step green approach and their application as mercuric ion sensor

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ABSTRACT

Carbon nanoparticles (CNPs) have been evolved as a promising candidate for the metal sensing applications due to their synthesis from naturally occurring and easily available non-toxic molecular precursors by green chemistry. A simple and one step procedure is reported here for the synthesis of CNPs from coconut milk by thermal pyrolysis at a temperature of 120–150 °C for 2–5 min without using any carbonizing or passivating agent. On pyrolysis the coconut oil is separated from the carbon rich residue and the residue when dissolved in water showed blue fluorescence under UV light. The CNPs produced are found to show an emission maximum at 440 nm when excited at 360 nm. Synthesis by green approach makes CNPs a promising substitute for the metal sensing applications. Series of metal ions which have a hazardous impact on the ecological system have been taken for the analysis and it is observed that the fluorescence of CNPs gets remarkably quenched by mercuric ions. Fluorescence quenching was studied using standard Stern–Volmer quenching model. Limit of detection was found to be 16.5 nM Hg^{2+} concentration.

1. Introduction

The scope of optical sensing has been broadened with the invention of highly fluorescent non-toxic carbon nanoparticles (CNPs) or carbon nanodots as the sensing probes [1–3]. Historically, starting from the natural organic dye to the recent semiconductor nanoparticles, the researchers have experimented with various advances in this area. The latest one among them was the use of semiconductor nanoparticles which shows some remarkable properties like high emission quantum yields, size-tuneable emission, chemical and physical stability, narrow spectral bands, possibility of surface modification for a specific sensing application, etc. [4]. But they suffer from the serious limitation of major health problems caused by the toxic effect of the heavy metal elements from which they are produced [5]. In this scenario, the non-toxic CNPs are benign alternative to semiconductor nanoparticles. Apart from the high photo-stability and lack of any cytotoxicity, the size and the excitation dependent photoluminescence are the versatile characteristics of these carbon nanoparticles. Sun and co-workers had synthesised carbon nitride dots from organic amines, N,N-dimethylformamide, CCl_4, etc. and these were successfully used for specialised catalytic applications [6–11]. Yu and co-workers had reported a lasing emission from carbon nanodots in organic solvents [12]. Hu and co-workers had prepared cabon nanodots from single chain polymeric nanoparticles and investigated their photoluminescence mechanism in organic solvents [13]. Various efforts were carried out to synthesise carbon nanoparticles from natural precursors. Peng and coworkers had used naturally occurring carbohydrates like glucose [14], Yang and co-workers used sucrose, and citric acid [15], and Sun and co-workers used pomelo peel [16], willow bark [17], etc. for the synthesis of carbon dots. It is reported that the optical, physical and chemical properties of produced CNPs are influenced by the molecular precursors used, methodology and the pre-treatment performed. Apart from optical sensing CNPs have found widespread applications in the areas of bioimaging [18,19], photocatalysis [20], optoelectronics [21], etc.

Synthesis of CNPs from naturally occurring and economically viable molecular precursors and their promising application towards various fields are important areas worth looking at. Application of fluorescent nanomaterials as a luminescent probe is the current trend. There are various reports on the use of the above mentioned CNPs for the metal sensing application [22]. Still the application of CNPs for the selective detection of metal ions is in the developing stage. The environmental and health hazards caused by the presence of toxic chemical waste containing heavy metals are of great concern for the modern industrial world. Presence of even traces of mercuric ions is a threat to the ecosystem due to their toxic nature [23]. Various sensitive and selective methods like atomic absorption spectroscopy, liquid chromatography, adsorptive stripping voltammetry, electrochemical, spectrophotometry and spectrofluorimetry

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are used for the qualitative and quantitative estimation of mercuric ions [24,25]. Among them, fluorescence spectroscopy has some added advantages such as low cost, facile sample preparation, high selectivity and easy detection [26]. So far many fluorescent probes especially based on carbon dots are employed for the detection of mercuric ions using various types of molecular precursors [27–31]. It has been reported that unmodified CDs can be used as a selective and sensitive fluorescence probe for rapid detection of Hg^{2+}. A good linear correlation was observed over the concentration range of 0–3 μM, with a detection limit of 4.2 nM based on a 3δ/slope [32]. However, many of the methodologies used for the synthesis of CNPs have the drawbacks of unfavourable reaction conditions like high temperature, prolonged reaction duration, usage of oxidising agents, the lack of aqueous solubility, etc.

Coconut milk which contains a high percentage of saturated fat (lauric acid) is a rich source of coconut oil. Coconut oil is extracted from coconut milk by thermal pyrolysis which is a traditional method to synthesise the virgin coconut oil. In the food industry normally the black residue obtained after the separation of coconut oil is discarded. Herein, we report a novel approach for the synthesis of CNPs from the waste by-product obtained by the thermal pyrolysis of coconut milk. This pyrolysis procedure does not involve any acid treatment or any surface passivating reagents. The obtained residue is found to be water soluble and the solution contains carbon nanoparticles of fluorescent characteristics. These CNPs are highly fluorescent and photostable, dissolves readily in water and other organic polar solvents and show excitation tuneable emission spectra. The efficiency of CNPs for metal ions sensing was tested using fluorescence quenching approach and the analytical characteristics are discussed.

2. Experimental

2.1. Materials

Coconut milk was extracted from grated coconut. This was used for the study without any preservatives. A.R. Grade Cupric nitrate ($Cu(NO_3)_2$), cobalt nitrate ($Co(NO_3)_2$), cadmium nitrate $Cd(NO_3)_2$, mercuric chloride ($HgCl_2$), nickel nitrate ($Ni(NO_3)_2$, lead nitrate $Pb(NO_3)_2$, manganese sulphate ($MnSO_4$) and iron sulphate ($FeSO_4$) were purchased from SDFCL and used as received without any further purification. Triply distilled water was used as a solvent throughout the experiment.

2.2. Instrumentation

The absorbance and fluorescence measurements were recorded using a UV–vis spectrophotometer (Shimdzu spectrophotometer) and spectrofluorimeter (JascoFP-8300), respectively. The absorbance of the sample was monitored between 200 nm and 600 nm. Excitation wavelength was kept at 360 nm and emission was recorded from 365 nm to 600 nm. The slit width for excitation and emission was kept at 2.5 nm for all the measurements. An Infrared spectrometer, FTIR-8400 (Shimadzu) was used to characterise the functional groups on the CNPs. A transmission electron microscope (TEM, Model TECNAI G2-20 U-Twin) with an operating voltage of 200 kV was used for the physical characterisation of the synthesised CNPs. The fluorescence life time measurements were carried out using a FL-TCSPC fluorescence spectrometer (Horiba Jobin Yvon Inc., France).

2.3. Synthesis

Fig. 1 shows the facile and one step synthesis of carbon nanoparticles from coconut milk in a cost effective and greener method. This involves the thermal pyrolysis of coconut milk under a mild temperature range of 120–150 °C for 2–5 min. On heating the sample, coconut oil was separated leaving behind a black residue. This residue obtained after the separation of coconut oil was air dried.

The dried sample was easily dispersed in water and an appreciable amount of the substance get dissolved in water and shows a yellowish brown colour as shown in Fig. 1C. The undissolved particles are removed by filtration and the centrifuged solution showed an appreciable blue fluorescence when exposed to UV light. These lyophilised CNPs were diluted with water till the appropriate concentration was reached and used for further analysis and sensing applications.

3. Results and discussion

3.1. Morphology and fluorescence characteristics

A few drops of CNPs aqueous solution is placed on a copper grid and dried and viewed under TEM. Fig. 2 shows the TEM and HRTEM images of the sample which contains spherical shaped carbon nanoparticles with an average size distribution ranging from 20 nm to 50 nm. This large size range could be the result of inhomogeneous pyrolysis process adopted in the synthetic step.

Fourier Transform Infrared spectroscopy was used to determine the functional groups present in carbon nanoparticles. FTIR spectrum of carbon nanoparticles produced from coconut milk is shown in Supporting information (Fig. S1). A characteristic absorption peak is observed at 3354 cm^{-1} which is due to –OH in the alcohol or phenol group. The stretching vibration bands at 2929 cm^{-1}, 1647 cm^{-1} and 1284 cm^{-1} are due to alkyl C–H bond, C–O bond in the amide groups and C–O bond in carboxylic acid, respectively. The bending vibration band of aromatic C–H bond was found at 887 cm^{-1}, suggesting the presence of alcohol or phenol, alkyl, carboxylic acid, amide and aromatic groups.

Fig. 3 shows the UV–vis absorbance spectrum of CNPs when dispersed in water. The absorption spectrum shows an edge at

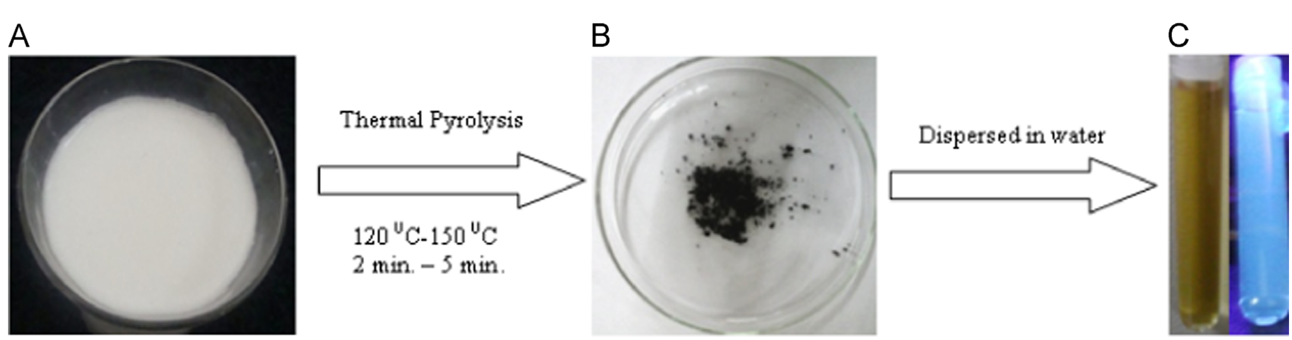

Fig. 1. (A, B) Digital images of the coconut milk and crude CNPs produced by the thermal pyrolysis of coconut milk, respectively. (C) Photographs of CNPs excited under daylight at 360 nm. (For interpretation of the references to colour in this figure, the reader is referred to the web version of this article.)