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Synthesis and characterization of carbon nanodots from jellyfish

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ABSTRACT

In a study which is first of its kind, florescent carbon nanodots (CNDs) were synthesized from jellyfish harvested off Cochin Sea using hydrothermal carbonization method. The synthesized CNDs were characterized by different techniques including, Ultraviolet–visible spectroscopy, Fluorescence spectroscopy, Fourier-transform infrared spectroscopy (FTIR), Differential scanning calorimetry (DSC), Atomic force microscopy (AFM), Transmission electron microscopy (TEM) and zeta potential. FTIR spectroscopic results showed that the CNDs were rich with C═O and C-O groups. Microstructure examination of CNDs using AFM and TEM, revealed the spherical shape of CNDs with about 50 nm diameter. A nylon net surface treated with 1% of CNDs shows good fluorescence under the UV light source. CNDs can have potential application in the area of tracing abandoned, lost and discarded fishing gear (ALDFG) in ocean and also in studying the fish behaviour either as attractant or deterrent.

1. Introduction

Jellyfish which is abundant in the marine and estuarine areas of Southeastern Arabian Sea is considered as major menace as they get entangled in the fishing nets [1] and the abundance of this resource has been recorded up to > 175 nos/100 m^2 from the South-west coast of India [2]. The climate change has seemed to trigger increase in the population of jellyfish which hinders fishing activity [3,4]. The major jellyfish species seen in the coastal waters of Kerala are *Crambionella orsini*, *Lychnorhiza malayensis*, *Chrysaora caliparea*, *Netrostoma coerulescens* and *Cyanea nozakii* [2]. Jellyfish are free swimming gelatinous zooplankton that are found mostly in coastal seas worldwide. In India, the occurrence of jellyfish bloom is a common phenomenon in estuarine and coastal waters. Especially, in recent years it was noticed that huge quantity of jellyfish is available during the post-monsoon season [2,5]. In India, the jellyfish catch has no market value and hence gets discarded in the sea especially since some of them allergic. However, recently some varieties of jellyfish (like Rhizostome) are being exported to destinations like China and South-east Asian countries for human consumption [5]. Effective management and sustainable utilization of jellyfish which is otherwise considered as menace will not only enhance earnings of the primary producer but also will help to manage the waste. Utilising jellyfish resources for manufacturing carbon nanodots paves an effective way of management since it has tremendous applications in the medical [6] and allied fields [7] apart from helping waste management [8].

Carbon nanodots are synthesized from natural and synthetic routes through hydrothermal carbonization, carbonization, microwave and sonolytic methods [9,10]. Natural materials discards were extensively employed for synthesizing carbon nanodots [11,12]. Carbon nanodots (CNDs) are fluorescent nano particle which have been widely used in cellular imaging, antimicrobial, antifouling, corrosion inhibition, catalysis, electronics, biosensing and other biomedical applications [13–17]. The major advantages of CNDs are environmental friendliness, good conductivity, low toxicity, high stability, excellent photostability, low photobleaching effect, free from heavy metals, cheaper to synthesize and emits multicolour fluorescence [18,19]. The green synthesis methods is most preferred practice as compared to physical or chemical process since it in very economical and eco-friendly. The present study attempted to synthesize CNDs from underutilised abundant fishery bycatch of Jellyfish, *Chrysaora* spp. through hydrothermal carbonisation method for the first time. The carbon nanodots were characterised using instrumental and chemical methods and were evolved as a surface coating over polyamide fishing net, which exhibited excellent fluorescence. The treated net can be utilised for attracting the fish or deterring the endangered species or marine animals.

2. Materials and methods

Jellyfish (*Chrysaora* spp.) was collected from trawl nets operated off-Cochin Sea by using ICAR-CIFT Research Vessel MFB Matsyakumari-II during post-monsoon season (Fig. 1). The *Chrysaora* spp. was found as

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the most abundant and widely distributed jellyfish species in the region. The jellyfish collected were washed with water and dried in an air oven at 60 ± 5 °C, crushed and the same was used for synthesis of carbon nanodots. Acetic acid was procured from CDH India and Milli Q Type I water was used for processing of samples. About 1 g of dried jellyfish + 20 ml of 1:1 acetic acid solution (glacial acetic acid:water) was added in a Teflon lined hydrothermal reactor and subjected to heating in a Nebertherm muffle furnace at 160 °C. The temperature was programmed from 0 to 160 °C with an increment of 4 °C per minute and kept at 160 °C for 7 h. After cooling, the contents of Teflon vessel were transferred to a 250 ml beaker and sonicated for 30 min. The brown coloured solution was filtered through a three layered Whatman 40 filter paper, instead of 0.2 μm filter to prevent clogging. The filtrate was stored in glass bottles at 4 °C.

The synthesized CNDs were characterized by using Shimadzu 2450 double beam UV-Vis spectrophotometer. Spectrofluorometric analysis of the samples were carried out using Shimadzu RF 6000 spectrofluorometer in the wavelength range of 200–800 nm with excitation increment of 20 units each. Further, the synthesized CNDs characterization was carried out using Thermo Nicolet iS10 Fourier transform infrared spectrometer (FTIR) in the wave number range from 650 to 4000 cm^{-1} using Zn-Se iTR accessory. Surface morphology of the material was analyzed using (JEOL JEM-2100 F) TEM at 200 kV. Diluted aqueous samples were dispersed over copper grid surface and analyzed using TEM. The surface topography of sample was studied using (Park System XE 100) AFM in non-contact mode using a silicon probe having < 10 nm tip. Differential scanning calorimetry was carried out using a Mettler Toledo DSC822e calorimeter. Particle size determination was carried out using the Malvern Mastersizer 3000 particle size analyzer [12,16].

Polyamide (nylon) fishing net having size 5 × 5 cm was exposed in the 1.0% nano CNDs solution over night to understand the adsorption characteristics of nylon. The CNDs adsorption over nylon fishing net was examined through UV-transilluminator (Syngene G:BOX F3, 230 V 50 Hz), also known as gel documentation system. The transilluminator software exhibit only black and white fluorescence images hence the fluorescence was photographed using mobile camera by opening the door of the instrument. All necessary precautions were under taken to avoid UV exposure to the personnel.

3. Results and discussion

Optimisation of the synthesis of carbon nanodots by altering various combinations of temperature and time revealed that optimum temperature was 160 °C for 7 h. Dark brown solution with green fluorescence CNDs were formed. The schematic representation of the process was shown in Fig. 1.

3.1. UV-Vis and fluorescence studies

The synthesized CNDs were delineated by UV–Vis spectroscopic analysis. The absorption of CNDs was recorded at 220 and 274 nm respectively due to the π - π * and n - π * transition. π - π * transition responsible for C═C and n - π * was due to the C═O, C-N and related functional groups. Jellyfish exhibited absorption at 209 nm and 280 nm, implied that jellyfish was transformed into CNDs (Fig. 2a). The data was comparable to previously reported CNDs from marine sources [12,16]. The absorption at 274 nm was low compared to 220 nm indicated higher the π - π * / n - π * ratio and hence expected the higher particle size. Jellyfish have low levels of fat, proteins, collagen and amino acids like glycine, lysine, arginine, glutamate and aspartate [20].

Fluorescence spectral analysis of CNDs exhibited emission maxima at 433 and 445 nm respectively at excitation 220 and 270 nm (Fig. 2b). The emission wavelength increased from excitation of 220–260 nm and almost stable upto 320 nm, further increase of excitation wavelength showed an increasing trend towards red side. The emission intensity maximum was showed at excitation 360 nm and lowest was at 220 nm (Fig. 2c). On increasing excitation wavelength from 220 to 280 intensity was increased marginally and then from 300 to 360 it was increased to maximum. CNDs exhibited intense greenish fluorescence and it was from the fluorophores emission at 433 and 445 nm. The emission at 445 nm was mainly from the surface states emission of CNDs [21]. The fluorescence or photoluminescence was excitation dependent emission and quantum yield of the CNDs will be higher in emission between 400 – 500 nm [22]. An additional emission peaks were shown in the blue region and it was not only shifting towards red region on increasing the excitation wavelength but also with increased intensity. This was mainly attributed to the molecular fluorescence of amorphous aggregate of CNDs [23].

3.2. Fourier Transform Infrared (FTIR) spectra

FTIR spectral characteristics of CNDs will provide the information on the presence of various functional groups and its nature. The FTIR spectral characteristics are presented in Fig. 2(d). The CNDs synthesized from jellyfish showed typical IR absorption at the wave numbers 1022 & 1088, 1292, 1444 &1416, 1624, 2872/2962, 3290 cm^{-1} which proved

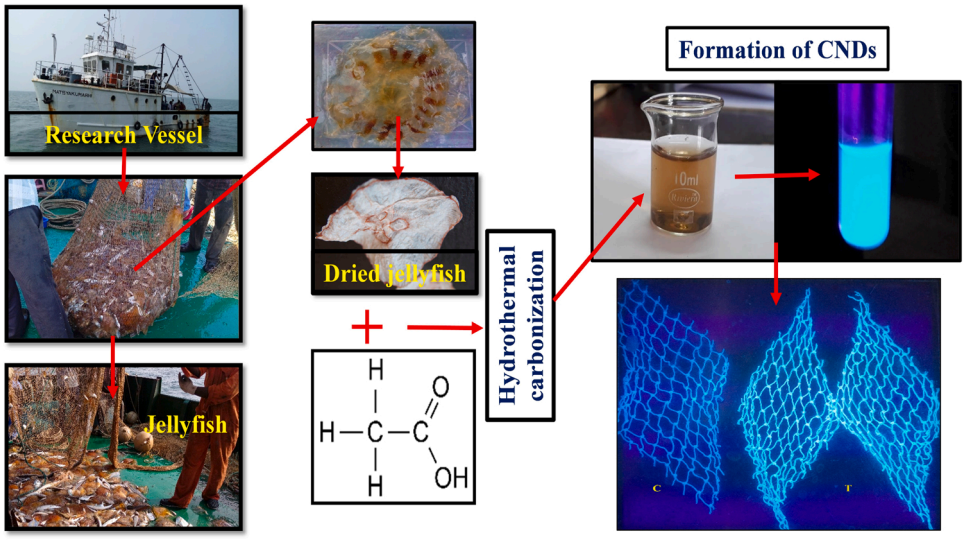

Fig. 1. Schematic for synthesis of carbon nanodots from jellyfish.

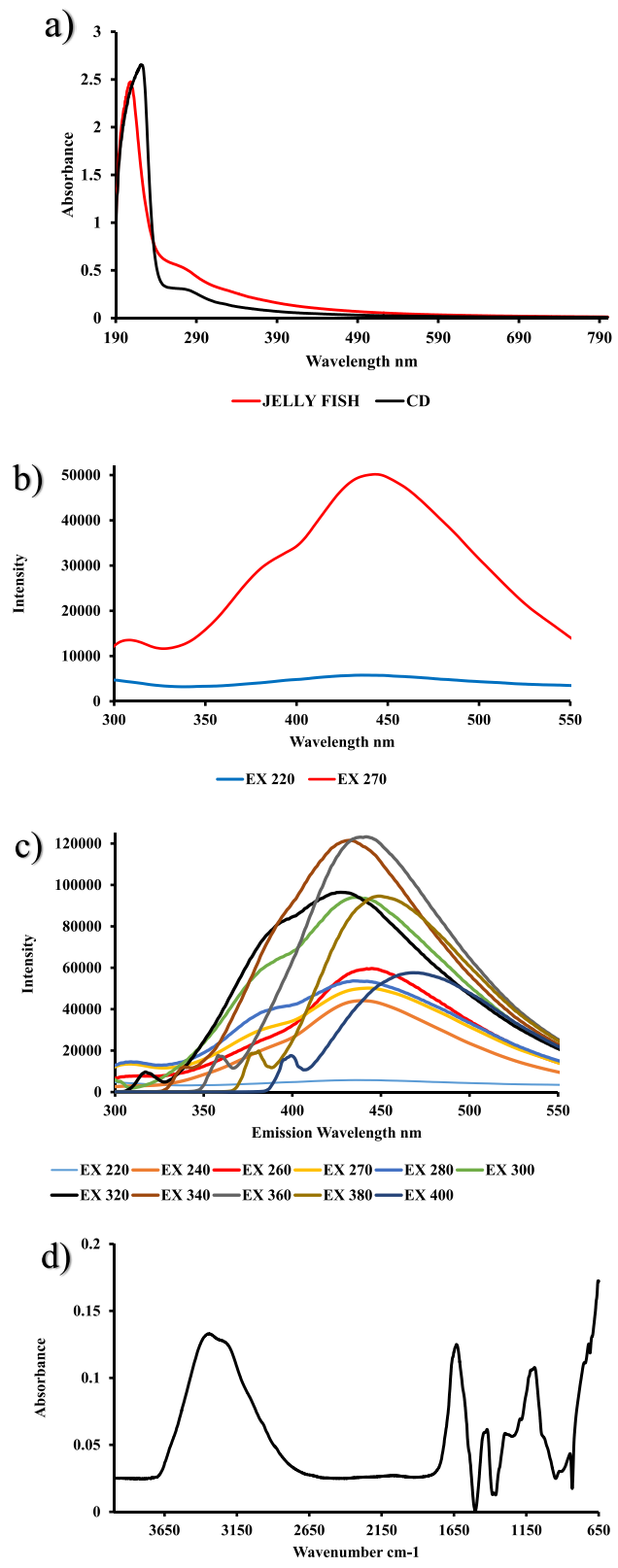

Fig. 2. UV-Vis spectra (a), fluorescence spectra (b and c) and FTIR of jellyfish (d).

the occurrence of functional groups such as C═C, C═O, OH, CN, C═C conjugated, C-H sym stretching and C-OH respectively in the given CNDs. According to Ding et al. [24], the C═O stretching vibrations of CNDs was at 1295 cm^{-1} and the reported value was at 1292 cm^{-1}. The IR band at 1657 cm^{-1} had shown N-H/ H bonded and band at 3213 cm^{-1} indicated the hydrogen bonded OH which further confirmed the presence of C-N …. O-H hydrogen bonding. Similarly, nitrogen doped CNDs shows O–H/N–H bonding was at 3357 cm^{-1}, C–H stretching vibrations were at 2945 and 2873 cm^{-1}, C–N at 1490 and 1451 cm^{-1}, C–O vibrations were at 1383 and 1351 cm^{-1}, and C–O–C vibrations were at 1210 and 1111 cm^{-1} were recorded [25]. However, Aji et al. [26] reported a clear band only at around 3455^{-1} cm for the pristine graphene and further no discernible bands were found. The results showed that the CNDs synthesized from jellyfish were comparable to IR absorption characteristics of CNDs prepared from other natural or synthetic methods. Comparing the intensities of different functional groups revealed that C-OH groups were comparatively higher.

3.3. Differential Scanning Calorimetry (DSC) Studies

DSC is a thermal analytical technique which measures the amount of heat energy that is required to increase the temperature of the sample as a function of temperature and can demonstrate a change in melting temperatures of nanomaterials depending on size [27]. The result indicated that at 138.69 ℃ the CNDs go through transition from crystalline state to amorphous state and the energy required for this endothermic process was about 67 Jg^{-1} shown in Fig. 3. DSC measured heats of combustion was 6.7 and 8.4 kJ g^{-1} respectively for carbon nano tube grown over Fe catalyst and after purification [28] and the higher energy was due to its unique carbon 2D structure. The results of the present study indicated the energy for endothermic process of CNDs were comparatively low probably due to its core containing varied atoms and functional groups.

3.4. Zeta Potential Studies

Zeta potential of the synthesized CNDs were analyzed to understand the colloidal stability of the particles and it was found to be + 18 mV for the CNDs synthesized from jellyfish. According to Zhou et al. [29] any value greater than 20 indicated the well dispersed colloidal system. The present study indicated the CNDs prepared from jellyfish was slightly aggregated nature.

3.5. Surface morphological characterization by AFM and TEM

Atomic Force Microscope illustrate the morphological features of the sample surface. In the AFM micrographs shown in Fig. 4a the particles were spherical clusters with multiple layers. The size of the CNDs was about 50 nm Ø. The mean surface roughness (Ra) and root mean square roughness (Rq) was about 0.69 and 1.04 nm respectively. The TEM micrographs showed that the carbon nanodot particles were spherical clusters and the diameter was about 20–50 nm (Fig. 4b). The formations of carbon nanodots were confirmed by TEM and AFM measurements. The prepared CNDs was in aggregated nature as evidenced from zeta studies hence the size was little higher.

3.6. UV transilluminator studies

Polyamide (nylon) based fishing gears were extensively used for harvesting ~~of~~ fish from marine and inland environments, owing to its low weight and cost effectiveness. Polyamide nettings were having low life span and gets discarded in the sea or shore and later it become a potential host for ghost fishing [30]. These ghost nets were difficult to trace in underwater. An attempt were made to treat the nylon net with 1% of CNDs and exhibited excellent fluorescence when it kept UV transilluminator as shown in Fig. 5. This study highlight the potential use of treatment of CNDs over the nylon nets so that it can traced while it lost in marine environment with less impact. It may also help to catch fish by exploiting the UV illumination over the CNDs treated net. Lou

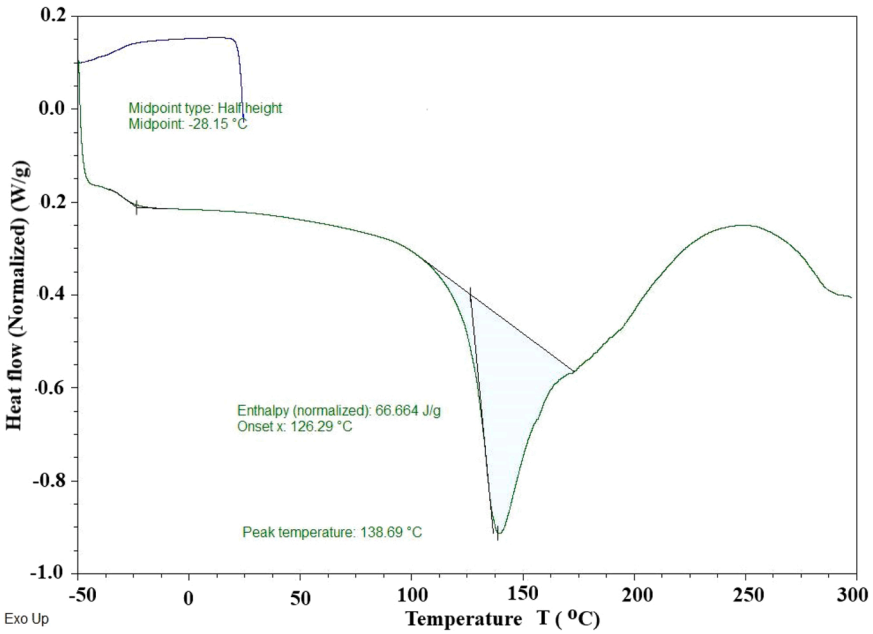

Fig. 3. DSC state of carbon nanodot sample.

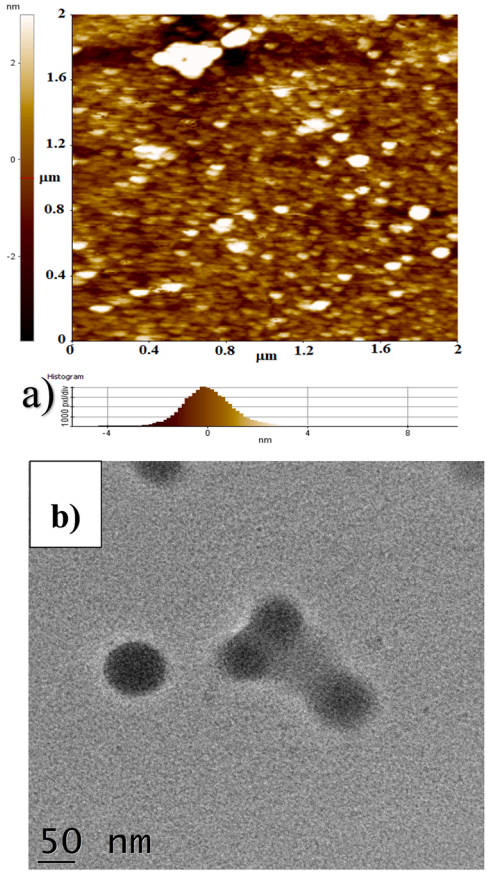

Fig. 4. AFM micrograph of carbon nanodots (a) and TEM micrograph of carbon nanodots (b).

et al. [31] described that the photoluminescence of CDs can be retained by applying pressure and the method has increased the fluorescence intensity under ambient conditions. Due to COVID situation and the subsequent restrictions, the authors could not carry out sufficient field evaluation studies to test the hypothesis and this can be tested in future research.

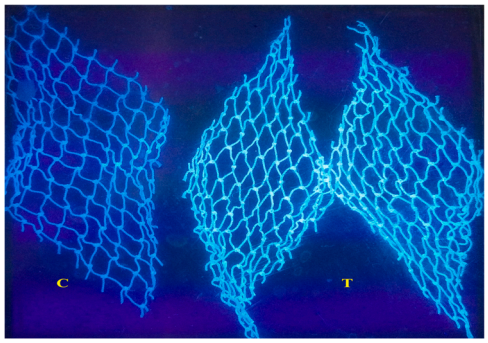

Fig. 5. Control (C) and treated nylon nets (T) under the UV transilluminator.

4. Conclusion

The present study highlighted the possibility of production of CNDs from jellyfish through hydrothermal carbonization method. Spectroscopic evaluation through UV-Vis spectroscopy divulges that jellyfish can be converted into carbon nanodots. The UV absorption of carbon nanodots was at 220 nm and 270 nm. Fluorescence spectra exhibited the emission maximum (λ em) at 340 nm & 460 nm when using an excitation wavelength (λ ex) of 220 nm and 270 nm respectively. FTIR examination revealed that the CNDs were rich with C═O and C-O groups but the presence of OH functional group was comparatively low. Zeta potential of the CNDs particles were positively charged (+18) and undergo phase change at 138.69 °C from crystalline state to amorphous state. The CNDs were spherical clusters having diameter of about 50 nm with multilayer having inter layer distance less than10 nm. The CNDs obtained are a potential candidate for sensor development and other medical applications. It has the advantage of inorganic metal free CNDs. It may also applied in netting materials and can be used to trace the abandoned, lost and discarded fishing gear (ALDFG) in ocean and can also be tested for fish behaviour studies.

CRediT authorship contribution statement

S. Chinnadurai: Conceptualization, Methodology, Investigation, Formal analysis, Writing – original draft, Writing – review & editing. **T. S. Krishnendhu:** Investigation, Writing - original draft. **P. Muhamed Ashraf:** Conceptualization, Methodology, Validation, Writing – review & editing. **Leela Edwin:** Writing – review & editing, Project administration.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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