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## Facile green synthesis of fluorescent carbon nanoparticles using spider silks

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### Abstract

Carbon nanoparticles (CNPs) have emerged as a promising candidate because of their interesting properties. They can be synthesized by chemical method as well as through green chemistry. Herein, we report a green synthesis approach for the CNPs from spider silk by pyrolysis at temperature 400 °C without using any carbonizing or passivating agent. The structural and optical properties of the synthesized CNPs have been characterized by using X-Ray diffraction (XRD), Raman spectroscopy, SEM (scanning electron microscope) - Energy Dispersive X-Ray (EDAX) analysis, UV-Visible and photoluminescence (PL) spectroscopy. The results obtained show that prepared carbon nanoparticles (CNPs) have a great potential for bio-sensing, bio-imaging, disease diagnosis, and other different optoelectronic device applications.

**Keywords:** carbon nanoparticles, spider silk, pyrolysis, photoluminescence spectroscopy

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### 1. Introduction

Nanotechnology (NT) is the most important research in the twenty-first century due to its wide range of applications from industries to biomedical including nanochemistry, nanoscience, nanomaterials, nanoelectronics, nanophysics, nanometrology, nano bionics, etc. [1]. Among them, nanoparticles can lead to new tools and technologies due to their unique compositions and functionalities [2]. Semiconductor nanoparticles produced from heavy metal elements show some excellent properties like high quantum yields, size-dependent emission properties, high chemical stability, and narrow spectral bands, etc. [3]. However, they are severely limited in terms of major health issues caused by precursor toxicity [4]. An alternative to this, recently nontoxic carbon nanoparticles (CNPs), a new category of carbon nanomaterial having ~ 2–100 nm size with interesting photoluminescence properties have developed to be one of the most extensive research topics nowadays [5]. There are several reasons why the scientific world is moving towards the CNPs. First, CNPs can be synthesized from naturally available carbon sources which are generally simple and economic. Second, the functionalization of the surface of CNPs is very easy, convenient, and adaptable. Third, CNPs have wonderful biocompatibility, excellent physical properties, and high aqueous stability. Fourth, the properties of CNPs can be increased by making a composite with other species. Recently, there is a great interest in the use of natural by-products as precursors for the synthesis of highly fluorescent non-toxic CNPs due to cost-effectiveness and biocompatibility [6]. The obtained CNPs possess some excellent properties like high quantum yield, low toxicity, broad absorption spectra, high fluorescent lifetime, high photostability, excitation-dependent emission intensity properties,

and chemical stability [7]. Due to its excellent properties, it has been extensively used in the field of bio-imaging, photocatalytic activity, drug delivery, optoelectronics, bio-sensing, fluorescent probes, nanomedicine, light-emitting diodes, and energy conversion/storage devices [8]. It can be synthesized by using different techniques such as arc discharge, plasma treatment, electrochemical oxidation method, laser ablation method, hydrothermal carbonization method, solvothermal method, ultra-sonication method, and microwave mediated method [9-10]. The physical, chemical, and optical properties of synthesized CNPs are governed by the methodology, molecular precursors, and pre-treatment. Several articles have recently been reported on the synthesis and characterization of CNPs using different routes from natural sources [11]. The fluorescence properties of CNPs depend on the surface defects which also include surface energy traps and excitons radiative recombination [12]. The chemical compositions of the natural precursors are the main reason for a different emission wavelength of fluorescent CNPs and it also determines the surface functional groups of the produced CNPs [13]. Methodologies followed for the preparation of CNPs have many drawbacks such as unfavorable reaction conditions like high reaction temperature, prolonged reaction time, lack of aqueous solubility, and use of strong oxidizing agents, etc. Therefore “green and eco-friendly” techniques are of great interest for the synthesis of CNPs due to their economic prospects and feasibility. Spider dragline silks (*Crossopriza lyoni*) contain a high amount of silk proteins. Because of their unique mechanical properties and exciting biological functionality, silk proteins have inspired the scientific community's interest. In this work, we report a novel approach for the synthesis of fluorescent CNPs by using the waste by-products spider dragline silks (*Crossopriza lyoni*) as green precursors by a simple pyrolysis method carried out at temperatures just above the onset of thermal degradation (that is,  $T > 250$  °C) without using any acid treatments or any surface passivating reagents [14]. The as-prepared CNPs have been characterized using an XRD, Raman spectroscopy, SEM with EDAX, UV-Visible spectroscopy, and Photoluminescence spectroscopy. The obtained CNPs are highly fluorescent and readily dissolves in water.

## 2. Experimental Section

### 2.1 Materials Required

Waste by-products of Spider dragline silks (*Crossopriza lyoni*) were collected from local houses in Rourkela, India. The chemicals used throughout this experiment such as Ethanol, Ethylene glycol, and Acetone were of AR grade (purity > 99%) purchased from Merck, India. Deionized water is used as a solvent throughout the experiment.

### 2.2 Synthesis

The synthesis of highly fluorescent CNPs from Spider dragline silks (*Crossopriza lyoni*) was carried out by a simple pyrolysis method. Collected waste by-products of Spider dragline silks (*Crossopriza lyoni*) were washed many times using ethanol, ethylene glycol, and acetone for further use. Then it was washed several times with deionized water for further purification. The washed spider dragline silks were dried in a vacuum oven at 70 °C for 24 hours. The dried samples were transferred into a quartz tube which was placed inside a tubular furnace for pyrolysis maintaining at temperature 400 °C for 4 hours and then switched off the furnace allowing it to cool down to room temperature. At room temperature, black products were obtained and it was mechanically grounded by using a pestle and mortar to recover fine powder. 0.25g. of the obtained powder was ultrasonically dispersed in 25 ml of deionized water to get the homogenous dark

brown solution. Then, CNPs were collected after the filtration of the dark brown homogenous solution by using a 0.22  $\mu\text{m}$  pore size syringe filter followed by drying in a vacuum oven at 60  $^{\circ}\text{C}$  for 7 hours.

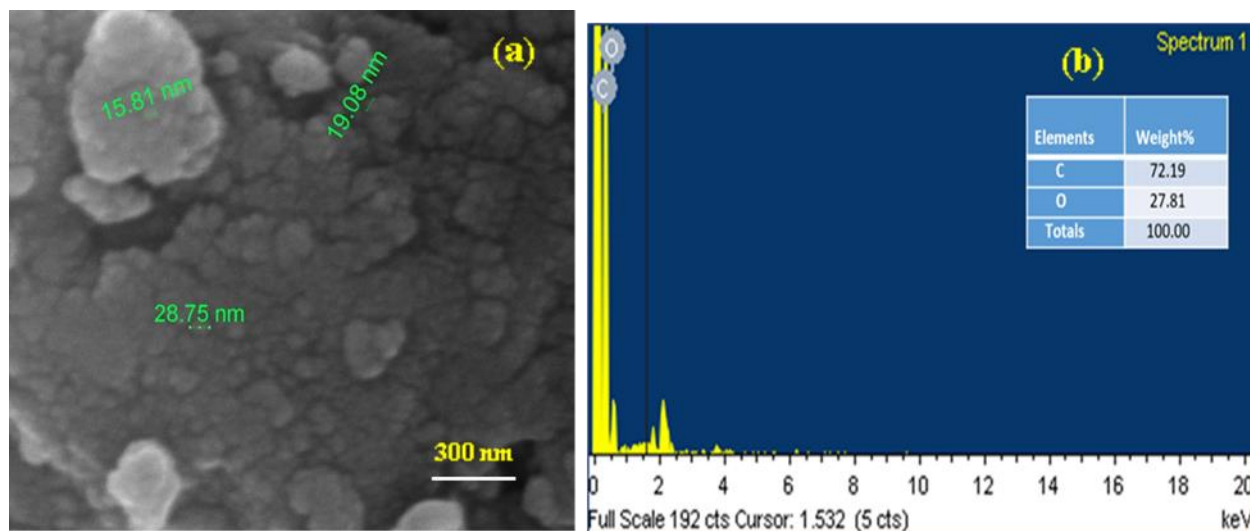
### 2.3 Instrumentation

The absorbance spectra of the synthesized CNPs were recorded using a UV-Visible Spectrophotometer (Shimadzu/ UV2450). The range of the wavelength for recording the absorbance spectra of CNPs was kept between 200 nm to 800 nm. Raman spectroscopy was performed to study the impurities as well as the chemical bonding and intramolecular bonds present in the sample. Raman spectra were recorded using a Raman spectrometer with a solid-state laser having a wavelength of 633 nm with a 50 mW power scan range 400-3000  $/\text{cm}$  (WITec Wissenschaftliche Instrumente und Technologie GmbH Model-XMB3000-3000). PL spectra were recorded by using PL Micro Raman Spectrometer (WITec Wissenschaftliche Instrumente und Technologie GmbH Model-XMB3000-3000). Powder X-ray diffraction (XRD) patterns were recorded using an X-ray Diffractometer (Bruker AXS D8 Advance Diffractometer) in the  $2\theta$  range of  $20^{\circ}$  to  $80^{\circ}$  to study the crystallinity of CNPs. Elemental composition and surface morphology of CNPs were studied using Scanning Electron Microscope (SEM)-EDAX (SEM: JEOL JSM- 6480 LV, EDS: Oxford Instruments)

## 3. Results and Discussion

### 3.1 SEM-EDAX Analysis of the CNPs

The surface morphology, average particle size, and elemental composition of as-prepared CNPs were analyzed by SEM and EDAX as shown in figure 1. Figure 1(a) shows the typical SEM images of CNPs with an average particle size of 15 nm – 30 nm in which most of the CNPs are spherical and uniform in size. The shape and size of as-prepared CNPs may vary due to the concentration profile [15].



**FIG 1.** (a) SEM images of CNPs and (b) EDAX spectrum of CNPs

The elemental composition of as-prepared CNPs was analyzed from the SEM-EDAX spectrum as shown in figure 1(b). The EDAX spectrum indicates the presence of carbon and oxygen in as-prepared CNPs.

### 3.2 XRD Analysis of the CNPs

The structural properties of the prepared CNPs were studied by the X-ray diffraction technique as shown in figure 2(a). A significant broad peak appears at about  $25.04^\circ$  which corresponds to the orientation of the (002) diffraction plane of  $sp^2$  structured graphitic carbon.

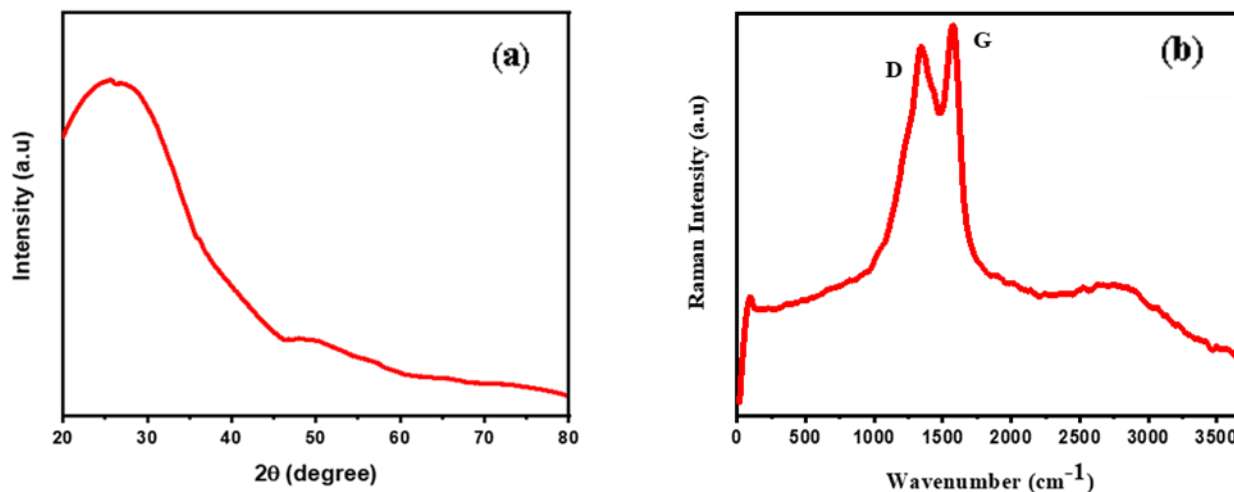


FIG 2. (a) XRD patterns of CNPs and (b) Raman spectra of CNPs

### 3.3 Raman Spectroscopy of the CNPs

The  $sp^2$  conjugated nature of as-prepared CNPs was studied by Raman spectroscopy as shown in figure 2(b). Two distinct peaks appear at  $1347\text{ cm}^{-1}$  and  $1567\text{ cm}^{-1}$  corresponding to the D band ( $sp^3$ ) and G band ( $sp^2$ ) respectively. The G band is attributed to the vibrations of  $sp^2$  bonded hybridized carbon atoms which corresponds to the  $E_{2g}$  mode in the 2-D hexagonal lattice of graphite. The D band is arising mainly due to the disordered structure  $sp^3$  bonded hybridized carbon cluster of graphite [16]. The intensity ratio of D-band and G-band ( $I_D/I_G$ ) was found to be 0.95 which correlates to the structural property of graphite.

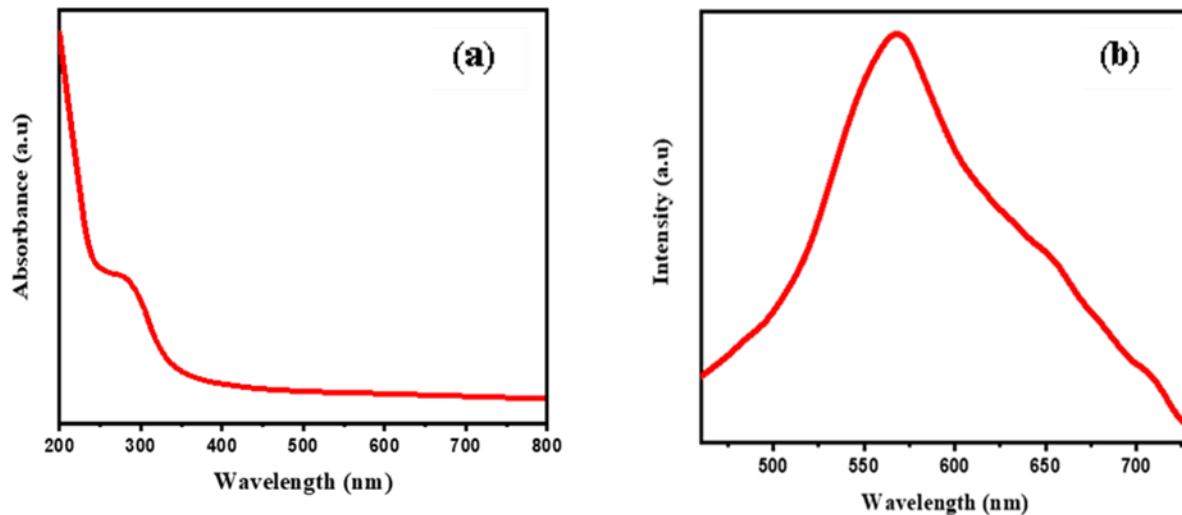
### 3.4 UV-Vis Spectroscopy of the CNPs

The optical properties of the CNPs were studied by UV-Visible spectroscopy as shown in figure 3(a). It shows a distinct peak at 277 nm, which is attributed to the  $\pi-\pi^*$  transitions of the conjugated C=C bonds in aromatic  $sp^2$  hybridization from the carbon core, indicating the presence of carbon nanoparticles [17-18].

### 3.5 Photoluminescence Spectroscopy of the CNPs

The as-prepared CNPs show a strong bright green fluorescence at 567 nm as shown in figure 3(b). The obtained broad peak in the PL spectra indicates the presence of large numbers of smaller particles that were excited at the UV-Visible range. The red-shift in the fluorescence emission spectra is mainly due to the presence of different-size carbon nanoparticles present in the sample and more oxygen content on their surfaces [19]. The excitation tunable emission property is the versatile characteristic of CNPs and it arises

mainly due to the size distribution, quantum confinement effect, and the presence of emissive traps on the surface. The number of surface defects will be higher if the degree of surface oxidation is increased [20].



**FIG 3.** (a) UV-Visible absorption spectra of CNPs and (b) Photoluminescence spectra of CNPs

#### 4. Conclusions

In summary, we report a simple, environment-friendly, and green approach to synthesize CNPs from spider silks (*Crossopriza lyoni*) which is economically cheap and naturally abundant precursors via simple pyrolysis method without using any passivating agents. The prepared CNPs show a bright green fluorescence and highly soluble in water without doing any surface modifications. The chemical bonds present in the domain range of synthesized CNPs were confirmed from the Raman spectroscopy. Further, the formation of CNPs was confirmed from the various characterization techniques like SEM-EDAX analysis, XRD, UV-Vis spectroscopy, and PL spectroscopy. The result suggests that the synthesized CNPs prepared by this approach could be promising candidates for bio-imaging, optoelectronics, and sensing applications.

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