

Synthesis of Carbon Dots from Spider silk: Conversion of waste to valuable product

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Abstract. Utilization of biomass as renewable and sustainable resource has attracted much attention of scientific community around the world. Herein, for the first time we report a green synthesis approach for carbon dots (CDs) from spider silk (*Crossopriza lyoni*) done by simple thermal pyrolysis at low temperature of 250°C. The synthesized CDs are comprehensively characterized by XRD, Raman, UV-visible and photoluminescence spectroscopy. The obtained higher band gap confirms the formation of CDs. The obtained results demonstrate that the prepared CDs have great potential application towards bio sensing, photovoltaic application, bio imaging and even disease diagnosis.

Keywords: Carbon Dots, Spider silk (*Crossopriza lyoni*), Pyrolysis, Raman spectroscopy.

INTRODUCTION

In recent years, a new emerging class of carbon nanomaterial like carbon dots (CDs), size ranges below 10nm have drawn major attention of scientific community owing to their outstanding fluorescence properties for various optoelectronic applications.¹ Many unique properties such as stable photoluminescence, high water solubility, chemical inertness, low toxicity, excellent biocompatibility and low cost makes CDs a potential material for photovoltaic devices, photo catalysis, cell imaging, fluorescent inks, medical diagnosis, chemical sensors, and biosensors. Their bio compatibility and cost effectiveness makes them more interesting in compared to traditional quantum dots. Carbonization of several organic compounds like glucose, sucrose, glycerol, citric acid, ascorbic acid, etc. have been utilized previously to produce CDs.² However, the time consuming and sophisticated nature of the mentioned approach limits their practical applications. There are many reported proves for CDs synthesis from carbonaceous materials like graphite and carbon nanotubes by physical methods like laser ablation, microwave-assisted methods, hydrothermal methods, ultrasonic treatment, arc discharge, plasma treatment and chemical methods like electrochemical oxidation, thermal oxidation, and vapor deposition of soot, wet chemical and electrochemical method. All this technique to synthesis procedures have been limited to smaller range spectral efficiency, low product yields. An alternative way to produce high yield CDs from commercially available food products, like bread, sugar, jiggery etc. due to the presence of carbohydrates.³ Now-a-days, researchers are finding an eco-friendly way to produce nanomaterial by using renewable resources as precursors for environmental concerns and the increasing rates of pollutions. Green synthesis of CDs from sources like prawn shells, cotton, orange peels, rice husk, lychee seeds, peanut skin, hair and peanut shells have been reported.⁴ Green chemistries is the only way towards sustainable processes which can be achieved by minimizing the waste produced, whose primary motto is to use non-toxic starting materials, environment friendly chemicals. The advantages of green synthesis of CDs are, it is less time consuming and doesn't require higher temperatures and also biocompatible in nature and cost effective. The parameters for altering size of CDs are the starting materials and duration of the process. In this work, for the first time, we have demonstrated the synthesis of fluorescent CDs using *Crossopriza lyoni* spider dragline silk (spider silk) as a carbon source by a simple

pyrolysis method carried out at temperatures just above the onset of thermal degradation (that is, $T > 250^\circ\text{C}$) without any chemical additives. *Crossopriza lyoni* has of great interest to the scientific community, due to the unique mechanical properties and interesting biological functionality of silk proteins.

EXPERIMENTAL SECTION

Spider dragline silks (*Crossopriza lyoni*) were collected from local houses and washed several times in a mixture of acetone, ethanol and deionized water for further uses. Spider dragline silks was drying in a hot air oven at 50°C for 6 hours. Then, the dried samples were placed in a furnace inside a quartz tube at 800°C for 4 hours. After cooling down to room temperature, black products were obtained and mechanically grounded with a pestle and mortar to a fine powder to recover final product.

RESULTS AND DISCUSSION

The optical analysis of the CDs was done by UV-Visible spectroscopy. The UV-Vis spectrum of the CDs exhibits a strong absorption peak at 275 nm, this peak was corresponded to the $\Pi-\Pi^*$ electronic transition of the C=C bonds of the aromatic rings shown in Fig. 1(a).⁵ The optical band gap of the as-synthesized CDs was calculated from the Tauc plot and estimated to be 3.91 eV, which confirms the formation of carbon quantum dots (CQDs) well matched with the reported literature (Fig. 1(b)).⁶

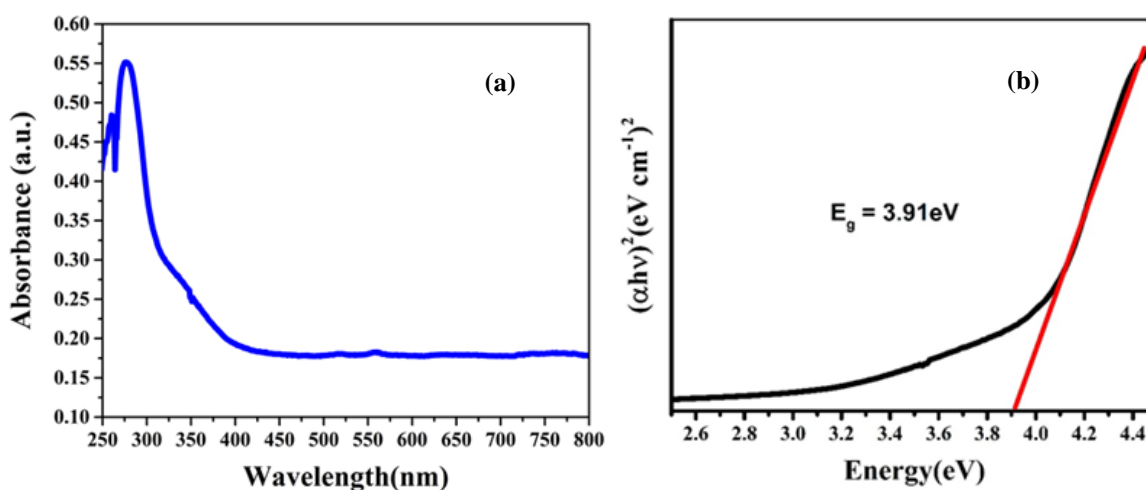


FIGURE 1. (a) UV-Vis absorption spectra of CDs (b) Tauc plot to estimate optical band gap of prepared CDs.

The structural characteristics of the synthesized CDs was studied by X-ray diffraction technique shown in Fig. 2(a). The diffraction pattern of CDs confirms that the synthesized CDs are crystalline in nature. A significant peak at $2\theta = 26.47^\circ$ correspond to the (002) diffraction orientation which corresponds to the planes of graphitic carbon (sp^2). The sp^2 conjugated nature of prepared CDs was verified by Raman spectroscopy. From this Raman spectrum the graphitic carbon was confirmed shown in Fig. 2(b). The Raman spectra showed two distinct peaks at 1341 cm^{-1} and 1580 cm^{-1} corresponds to D band (sp^3) and G band (sp^2) respectively well matched with literature values. The G band arises from the vibrations of sp^2 bonded carbon atoms corresponding to the E_{2g} mode in 2-D hexagonal lattice of graphite. The D band is associated with the vibrations of dangling bonds in the termination plane, corresponding to the disordered structure in the sp^3 cluster of graphite.⁷ The relative area of intensity of D-band and G-band (I_D/I_G)

correlates the structural property of graphite. Here in this case, I_D/I_G was found to be 0.9 which indicating the nano-crystalline graphitic nature of prepared material.⁸

The prepared CDs exhibited an excitation-dependent photoluminescence (PL) emission spectrum obtained by 355 nm laser excitation (Fig. 2(c)). It was seen that that the prepared CDs exhibited strong green fluorescence at 557 nm, but the CDs solution was colorless in daylight. The variation in PL intensities is mainly due to the size differences in CDs. The spectra with a peak at higher intensity indicate the presence of large number of smaller particles which were excited at UV-Visible range. The fluorescence emission is closely related to the surface state of CDs, which includes the degree of surface oxidation and surface functional groups.⁹ The red-shifted emission of CDs is closely related to the oxygen content on their surface. The higher the degree of surface oxidation, the greater the amount of surface defects.¹⁰

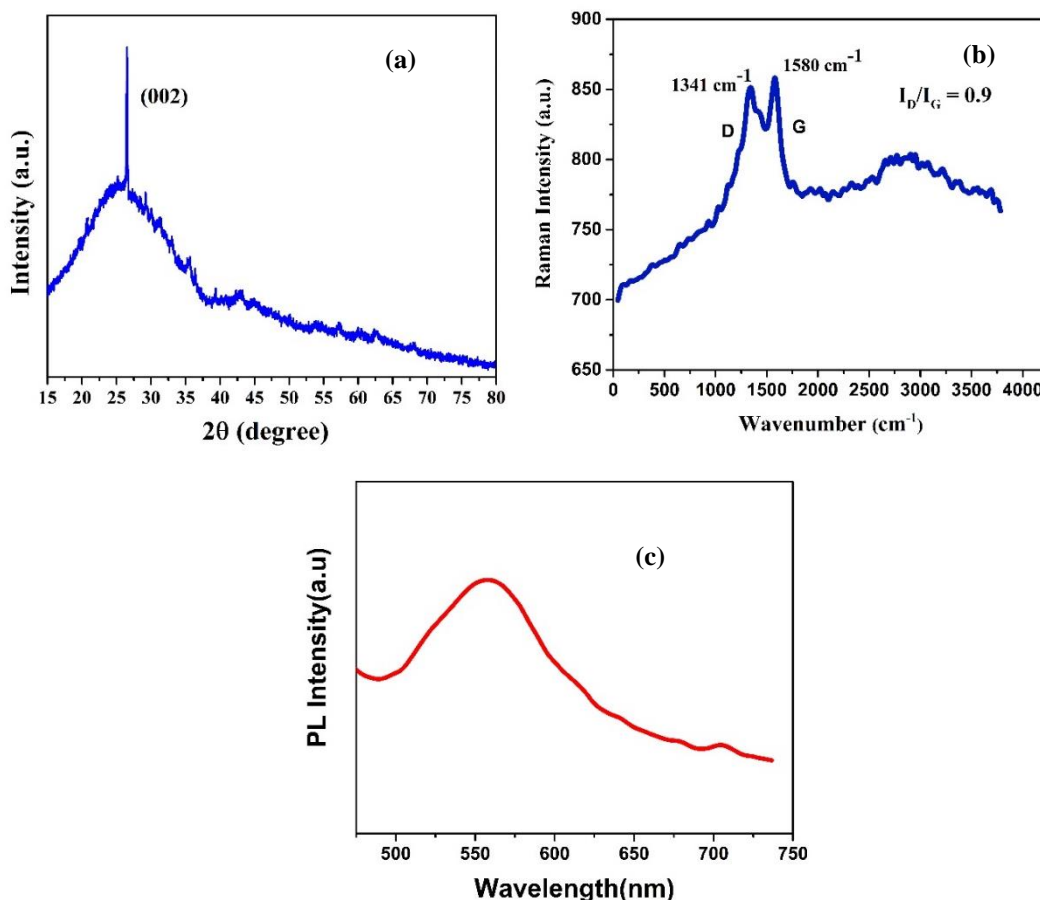


FIGURE 2. (a) X-ray diffraction pattern, (b) Raman spectra, and (c) photoluminescence (PL) spectra as synthesized of CDs

CONCLUSION

In summary, for the first time, we have reported a simple, economic, environment friendly, and green approach to synthesize CDs from spider silk (*Crossopriza lyoni*) via pyrolysis method in the absence of any other toxic chemicals. The prepared CDs exciton dependent intensity, strong fluorescence intensity and highly soluble without doing any further surface modifications. The crystalline nature of prepared CDs has been confirmed from diffraction pattern. From Raman spectroscopy analysis, the chemical bonds present in synthesized CQDs confirms the formation

and presence of CDs in nano-crystalline domain range. The formation of CQDs is corroborated from the UV-Visible and PL spectroscopy analysis and the obtained band gap energy i.e. 3.91eV is estimated from Tauc plot, which shifts towards higher energy confirming the formation of CQDs. Moreover, the prepared CDs prepared by this approach could be a possible candidate for future optoelectronic applications.

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