

FACILE MICROWAVE –ASSISTED SYNTHESIS OF CASEIN DERIVED CARBON NANODOTS

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Abstract

Belonging to the carbon family, yet standing apart, carbon nanodots are materials with excellent properties. Among them, they are well known for their attractive optical properties. The insight into this outstanding strength has resulted in the discovery of unique design of materials. These nanodots can be prepared via various methods to obtain a good optical response. In our research, we synthesized them using a microwave reactor, which is simple, fast and productive. As a carbon source casein, a low-cost precursor was used. Since this is a protein composed of amino acids, no additional passivation was required. Polyvinylpyrrolidone was used as a stabilizer for the nanodots. The synthesis was carried out at 200 °C for 30 minutes. The color change of the resulting solution to orange brown indicates the formation of carbon nanodots. These nanodots were filtered and dialyzed to be used for further characterizations. The carbon nanodots were spherical with the average size of about 9.7 nm. They showed a strong blue emission in the visible region with an appreciable quantum yield. One of the important characteristics of this method is the availability of reasonably good product yield. The prepared carbon nanodots have potential applications in the field of electrochemistry, optoelectronics and biological imaging.

Keywords: Carbon nanodots, casein, microwave reactor, Polyvinylpyrrolidone

1. INTRODUCTION

In the recent decade, carbon nanodots (CNDs) have emerged as excellent luminescent materials. Since these materials manifest extraordinary merits, they are the hot topic of research studies. CNDs are materials with dimensions less than 10 nm. They were discovered in 2004 during the purification of single-walled carbon nanotubes [1]. Because of their alluring properties, CNDs are extensively used in applications like bioimaging [2], light emitting diodes [3] and sensing of metal ions [4]. Moreover, researchers all around the world have discovered different methods for synthesis such as hydrothermal [5], microwave irradiation [6] and laser ablation [7]. The structure of CNDs contains a mixture of sp^2 and sp^3 hybridized carbon atoms with an amorphous core. To enhance the optical properties, their surface is usually passivated with various functional groups or heteroatoms. Furthermore, depending on the surface structure, hydrophilic [8], hydrophobic [9] and amphiphilic [10] CNDs can be obtained.

Amongst all the properties, the optical properties have been widely investigated. The core and surface states play a crucial role in the emission. Recently, different kinds of carbon precursors have been used to obtain better photoluminescence (PL) response [11,12]. Even though the mechanism of PL emission is still under debate, the three most important mechanisms include quantum confinement, surface state and molecular fluorophore [13]. CNDs usually follow the trend of excitation dependent PL spectra with strong emission in the blue region, whose intensity decreases with the red shift. This red shift in the PL spectra is observed due to high surface oxidation [14].

To further investigate the optical property, fluorescence lifetime decay studies are carried out, which helps in understanding the potential applications of CNDs. Multi-exponential decay of these studies is considered as a

fingerprint of heterogeneity which is obtained from dot-to-dot differences in excited-state lifetimes [15]. Another important optical property is the fluorescence quantum yield. One group of researchers synthesized CNDs using citric acid and urea and studied the factors affecting the quantum yield. They discovered that high temperature and longer reaction time lead to a decrease in the quantum yield [16]. Achieving high fluorescence quantum yield with a good product yield has always been a challenge.

Even though CNDs have been synthesized from different precursors, their chemical, structural and optical properties have not been clearly understood yet. In our work, we synthesized CNDs from a protein named casein. Since casein is rich in amino acids, doping was avoided. The structural, chemical and optical properties of the synthesized material were studied using transmission electron microscope, fourier transform infrared spectroscopy, UV-Vis spectroscopy and photoluminescence spectroscopy.

2. EXPERIMENTAL

2.1. Materials required

MPC 85 Micellar Casein was purchased from a local seller in the Czech Republic. Polyvinylpyrrolidone (PVP) was bought from Sigma Aldrich. Solvents like ethylene glycol and isopropanol were procured from PENTA, Czech Republic. All reagents were used without any further purification.

2.2. Synthesis of casein based carbon nanodots

The synthesis of casein based carbon nanodots (CNDs) was carried out using a microwave reactor. In the typical synthesis, 0.1 g of casein and 0.2 g of PVP were taken in two separate beakers and dissolved in 20 ml of ethylene glycol separately using a sonication probe. Then, the two solutions were mixed and poured in a teflon lined container to be kept in the microwave reactor. This reaction mixture was maintained at 200 ° C for 30 minutes with 100% (600 W) power. After 30 minutes an orange-brown solution was obtained. This solution of carbon nanodots was filtered using a 0.22 μm membrane and dialyzed against water using a dialysis bag (3.5 KD) for two days to remove the excess of PVP. The resulting solution was freeze dried and the final product (40mg) was obtained.

2.3. CNDs characterization

The synthesized CNDs were characterized using various characterization techniques. The Ultraviolet-Visible (UV-Vis) absorption studies were carried out on Perkin-Elmer Lambda 1050 spectrometer. The photoluminescence (PL) emission spectra was recorded on FLS920, Edinburgh Instruments (excitation laser 332.2 nm, Xe lamp excitation 515 nm). The Fourier Transform Infrared (FTIR) spectra were obtained from Thermo Scientific Nicolet 6700 spectrometer utilizing the ATR method with the diamond crystal (4000–400 cm^{-1} , resolution 2 cm^{-1} , 64 scans). Transmission Electron Microscope (TEM) studies were carried out on the JEOL JEM 2100 microscope operated at 300 kV (LaB₆ cathode, point resolution 2.3 Å equipped with OLYMPUS SYS TENGRA camera (2048 × 2048 pixels)). The particle analysis was carried out using Image J software.

3. RESULTS AND DISCUSSIONS

The morphology and the size of the synthesized CNDs was confirmed through TEM characterization. The TEM image is shown in **Figure 1**. As can be seen, the particles are randomly distributed with a spherical shape and of different sizes. The average particle size of the CNDs was found to be around 9.7 nm.

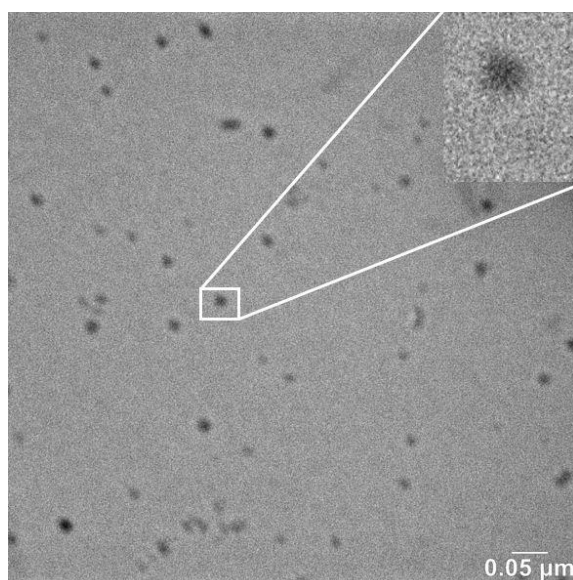


Figure 1 TEM image of CNDs

Figure 2 provides the FTIR spectrum of the CNDs. As shown, the spectrum indicates the presence of various functional groups. The peak at 3357 cm^{-1} shows O-H and N-H stretching vibrations. Characteristic casein peaks were observed at 2920 cm^{-1} and 1850 cm^{-1} due to the appearance of symmetric and asymmetric stretching of CH_2 [17]. The existence of C=O stretching vibrations can be found at 1656 cm^{-1} , O-H bending vibrations are seen at 1423 cm^{-1} . The peaks present at 1288 cm^{-1} and 1043 cm^{-1} indicate C-N stretching and C-O stretching, respectively.

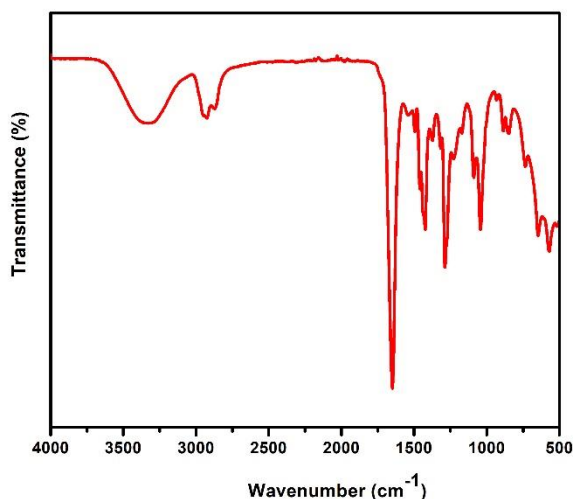


Figure 2 FTIR spectra of CNDs

The optical studies help in understanding the electronic transitions happening in CNDs. Therefore, we have investigated the absorption and emission spectra. When the CNDs were illuminated with a UV lamp of wavelength 365 nm, a blue color solution was observed. **Figure 3 (a)** shows the UV spectra of Casein based carbon nanodots. As can be seen, a peak is observed at 278 nm. This peak is due to the $\pi\text{-}\pi^*$ transition of the aromatic C=C bond [18]. The PL emission spectra of the CNDs excited from 320-420 nm is shown in **Figure 3 (b)**. As revealed by the graph, an initial increase in the peak intensity is observed, followed by a

gradual decrease. The presence of surface defects due to a high level of surface oxidation causes emission to shift to longer wavelengths [19]. When the CNDs were excited at 350 nm, the highest peak was obtained at 427 nm, which appears to be in the region of blue emission. The polydispersity of the sample can be one of the factors for the formation of excitation dependent emission spectra.

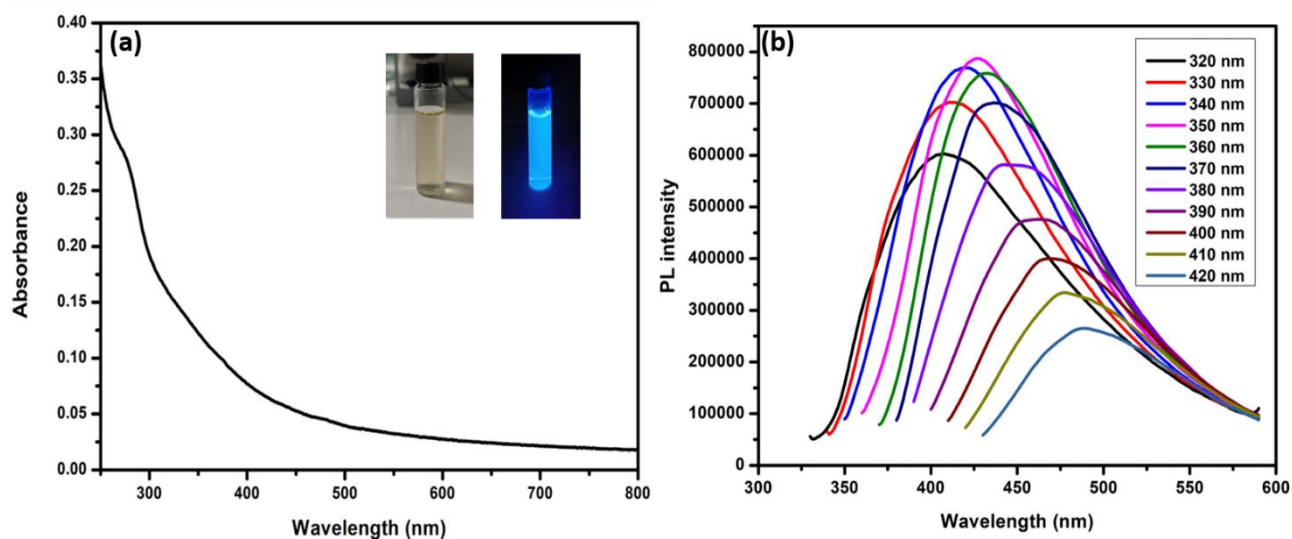


Figure 3 a) UV absorption spectra of CNDs **b)** PL emission spectra of CNDs

The quantum yield of the CNDs with water as a reference was found to be 4 %, which is comparable with those reported in the literature [17,20].

4. CONCLUSION

In summary, the study has reported a successful synthesis of CNDs using a simple and easy approach. The resulting CNDs are spherical in shape, they exhibit excitation dependent photoluminescence spectra with a red shift, indicating the heterogeneity of the sample. A strong blue color emission indicates the typical characteristic of the material. Compared to all the other methods, this technique is less time consuming and easily reproducible with a good yield. The bare casein CNDs show considerably less quantum yield than expected, hence it is concluded that in the next step, passivation is necessary to obtain an increase in this property. Passivating these CNDs with various functional groups or dopants can lead to their application in numerous arenas like biomarkers, optoelectronics, drug delivery and photosensitizer.

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