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Excitation-Dependent and pH-Sensitive Fluorescence Emission of Carbon Quantum Dots from Whey as Precursor

Ahmet Burak İLTER[1]
Selin AYDIN[2]
Aslı YILMAZ[2]
Mehmet YILMAZ[1,3]

[1]Atatürk University, Department of Nanoscience and Nanoengineering, Erzurum, Türkiye
[2]Atatürk University, Department of Molecular Biology and Genetics, Erzurum, Türkiye
[3]Atatürk University, Department of Chemical Engineering, Erzurum, Türkiye

ABSTRACT

Fluorescent carbon nanoparticles or carbon quantum dots, a novel type of nanomaterials, have been introduced with their unique chemical, optical, and biological properties. Due to their high biocompatibility and non-toxicity, low cost, and unique emission properties, carbon quantum dots have become the focus of attention in nanotechnology in a short time. Thanks to these features, they provide opportunities for use in many fields such as biotechnology, bioimaging, drug release, biosensors, photocatalysis, and, solar cells. In addition to these advantages, they may offer excitation wavelength-dependent properties and the pH-sensitive photoluminescence mechanism. In this study, we present a simple yet environmentally friendly method to produce carbon quantum dots from whey, an important dairy waste. For this, carbon quantum dots were synthesized by hydrothermal synthesis using whey as the precursor for 24 hours at 220°C. The fabricated carbon quantum dots exhibited a bluish-white emission under ultraviolet light with an excitation-dependent property. Also, as the pH value increased, the fluorescence activity decreased accordingly without any remarkable shift in absorption maxima indicating the potential application of carbon quantum dots as pH sensors in various chemical and biological systems.

Keywords: Carbon quantum dots, excitation-dependent emission, whey, hydrothermal synthesis, pH sensor

INTRODUCTION

Carbon quantum dots (CQDs) are novel carbon-based nanomaterials that have been proposed in the last two decades as an alternative to their conventional counterparts such as inorganic semiconductors and fluorescent dyes.[1,2] Typically, CQDs are in the range of 2-15 nm with a carbon-based skeleton and various functional groups on the surface.[3–6] Many parameters including chemical content, nanoparticle size, and distribution as well as the type of surface groups intensively govern the physical, chemical, and resultant optical nature of CQDs.[7–9] With their unique structures, CQDs offer advantages in terms of high fluorescence activity with photostability, low cytotoxicity, high biocompatibility, high solubility, flexible surface structures, easy functionalization of the surface structure, chemical stability, and low cost.[4–6,10,11] Thanks to these unique properties, CQDs are widely employed in many fields such as chemical sensing, bioimaging, photocatalytic applications, and nanomedicine.[12–20]

To date, significant progress has been performed regarding the production and applications of carbon quantum dots. Both top-down and bottom-up approaches have been utilized for the production of CQDs. In the case of the top-down approach, the size of carbon-based raw material is reduced to the nanoscale after the application of chemical or mechanical processes including electrochemical oxidation, laser ablation, arc discharge, and high-energy ball milling.[21–25] These techniques require high energy and expensive and complicated devices and lead to poor control over the size and content of the fabricated CQDs which are the major drawbacks of the approach that must be considered. In the bottom-up approach, atomic or molecular structures are used to fabricate materials on the nanoscale. In this context, various strategies including microwave-assisted, chemical vapor deposition, combustion, ultrasonic-assisted, solvothermal, and hydrothermal methods have been widely utilized for the fabrication of CQDs.[26,27] However, the hydrothermal method is the most preferred method due to its low cost, simplicity, and high reproducibility.[26,27] In the hydrothermal method, the processes are carried out in an aqueous solution in a closed system at a relatively high temperature (>100°C) and pressure (>1 atm). In general, the optical and chemical structure of resultant CQDs can be manipulated by the main process parameters such as synthesis temperature and time, initial pH, and the type of precursor.

So far, various organic materials including urea, lactic acid, and dopamine have been employed in the fabrication of CQDs via hydrothermal synthesis.[4–6] This approach dictates the usage of the precursors

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Corresponding author:
Mehmet YILMAZ
E-mail: nano.yilmaz@gmail.com

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with high costs. Recently, the employment of biomass waste from various sources such as agriculture and livestock, organic domestic waste, forestry, and related industries has been proposed as precursors of CQDs.[28–30] These sources provide significant advantages in terms of low-cost, renewable, and, environmentally friendly material with easy access. Also, this approach eliminates the treatment of industrial waste.

Herein, we propose the usage of whey as industrial waste from the dairy plant in the fabrication of CQDs via hydrothermal synthesis. We detected that the resultant CQDs exhibited high photoluminescence (PL) activity with pH-sensitive fluorescence nature in a wide pH range (4-9) indicating their potential applications in monitoring pH in various chemical and biomedical systems.

MATERIALS AND METHODS

For the synthesis of CQDs, whey was obtained from a local dairy plant in Erzurum as the precursor. Then, the whey was passed through filter paper (ISOLAB, 125 mm) to eliminate the suspending impurities. The appropriate amount of the whey was mixed with 10 mL of distilled water. The mixture was transferred to a Teflon-coated stainless steel reactor (40 mL) and kept in the oven for 24 hours at 220°C. At the end of the period, the reactor was cooled to room temperature and centrifuged at 13,000 rpm for 1 hour to remove aggregate structures.

An Agilent Cary Eclipse fluorescence spectroscopy (Santa Clara, Calif, USA) was used to determine the fluorescence nature of the prepared CQDs. Absorption spectra were collected by using ultraviolet-visible (UV-vis) spectroscopy (Shimadzu, UV-1800, Kyoto, Japan). The size and morphology of the particles were characterized using transmission electron microscopy (TEM, Hitachi Hightech HT7700, Tokyo, Japan). The pH of the CQDs was measured via a Mettler Toledo pH meter (Columbus, Ohio, USA).

RESULTS AND DISCUSSIONS

In this study, we basically aimed to determine the fluorescence nature and potential applications of CQDs obtained from whey, an important dairy waste product. For this, we employed the hydrothermal synthesis approach at 220°C for 24 hours. After the purification step, we collected fluorescence spectra at different excitation wavelengths and UV-vis absorption spectra (Figure 1). It was observed that the increase in excitation wavelengths in the range of 280-600 nm led to an obvious red shift in the fluorescence maxima from 478 to 622 nm (Figure 1A). This phenomena obviously indicate the excitation-dependent nature of the resultant CQDs. Also, the optical image of nano-colloid suspension exhibited a pale yellow color in daylight due to the carbonization of substances in whey (see inset in Figure 1A). Also, under a UV lamp (365 nm), the CQDs emitted a strong and bright bluish-white emission (see inset in Figure 1A). In UV-vis absorption spectra (Figure 1B), a weak peak maximum was observed at 291 nm indicating π-π^* transition. This transition can be attributed to the presence of aromatic C-C bonds in the structure of CQDs.[4–6] It seems that the whey as a precursor used for this synthesis was sufficiently carbonized to produce CQDs with high and excitation-dependent fluorescent activity.

After evaluating the optical properties, we collected some TEM images to analyze the morphology and size distribution of CQDs (Figure 2). From TEM images, we detected irregularly shaped carbon nanomaterials with amorphous structures (Figure 2A). The particle size distribution analysis showed that the size ranged

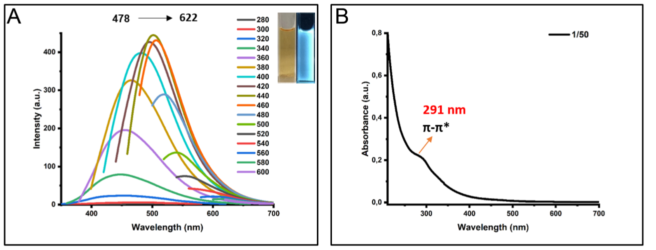

Figure 1. Fluorescence spectra of carbon quantum dots at different excitation wavelengths (A) (inset, optic images under daylight (left) and a 365-nm UV light (right)) and UV-vis absorption spectra (B). UV, ultraviolet; vis, visible.

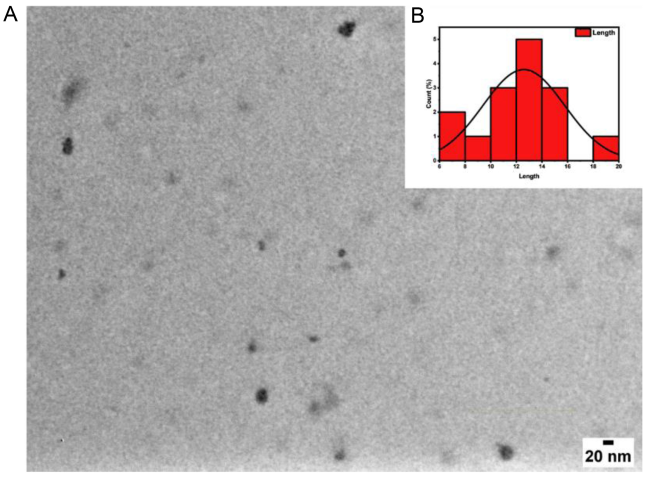

Figure 2. TEM image (A) and histogram plot (B) of CQDs showing particle size distribution. CQDs, carbon quantum dots; TEM, transmission electron microscopy.

from 8 to 20 nm with an average of 13.3 nm. The wide size distribution of CQDs may create a wide fluorescence emission for almost all visible ranges and resultant bright bluish-white emission. This issue must be furtherly investigated which will be the topic of our next study.

Finally, we checked the PL activity of CQDs over a wide pH range (4-9). We collected fluorescence spectra and their normalized intensity at different pH values (Figure 3). The maximum PL activity was observed for a pH value of 4. As the pH increases, the PL intensity decreases accordingly without any remarkable shift in absorption maxima. Considering the pH range of living organisms, we may conclude that the proposed CQDs can be employed as pH sensors for a given pH range. In our next study, this application of these nanosystems will be tested to determine pH-based imaging of living cells.

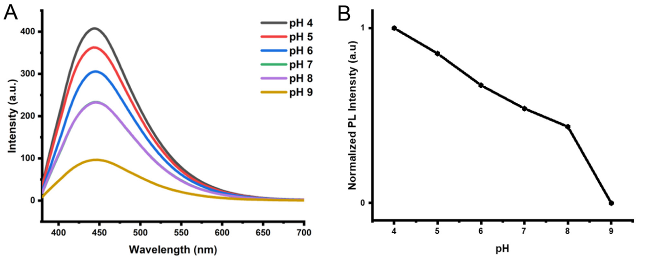

Figure 3. Fluorescence intensity of carbon quantum dots at different pH values (A) and normalized PL intensity (B). PL, photoluminescence.

CONCLUSIONS

In this study, we fabricated CQDs with excitation-dependent nature via a simple and low-cost hydrothermal method using whey as industrial waste from the dairy plant. With the increase in excitation wavelengths, an obvious red shift in the fluorescence maxima from 478 to 622 nm was observed probably due to the wide size distribution of CQDs with a wide fluorescence emission for almost all visible ranges and resultant bright bluish-white emission. As the pH of the CQD suspension increased, the PL activity decreased accordingly without any remarkable shift in absorption maxima. We envision that the proposed CQDs may be employed as pH sensors to monitor pH in various chemical and biomedical systems.

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