Synthesis of Carbon Quantum Dots from Food Products by Hydrothermal Carbonization Method

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Abstract. The article describes the preparation and filtration of a solution containing carbon quantum dots. In this paper carbon quantum dots were obtained from food products, cheap and environmentally friendly hydrothermal carbonization method, without using toxic chemicals reagents. Moreover, to study the optical properties of the carbon quantum dots UV-VIS absorption were carried out. The maximum absorbance was determined in the range of λ~377 to ~408nm. Furthermore, carbon quantum dots were found to emit green light.

1. Introduction
Carbon Quantum Dots (CQDs) are a new class of carbon nanomaterials, typically less than 10nm in size. Moreover, it is considered that CQDs structure consists of a graphite core with surface functional groups. Their discovery was documented in 2004, until 2006 they received the name "carbon quantum dots". Since then, CQDs have attracted significant and growing interest due to their unique properties that enable their use in many branches of science. The most important of them are photoluminescence, biocompatibility, good water solubility, photostability and low toxicity. Therefore, research is being carried out on the use of CQDs in, among others, bioimaging, drug delivery, photocatalysis and photovoltaic devices. Furthermore, they are also used as biosensors (e.g. for visual glucose monitoring) [1-3]. The first methods of synthesis used the strong influence of energy on the carbon source, which resulted in the formation of fluorescent carbon nanoparticles. An example of this approach is laser ablation [4-6]. Nowadays, CQDs synthesis methods are divided into two main groups: bottom-up and top-down. Bottom-up methods rely on the synthesis of CQDs from molecular precursors, whereas top-down methods rely on breaking down larger carbon structures [1]. During the synthesis of CQDs, there are three basic problems to consider: carbonaceous aggregation during carbonization, control of size and homogeneity, surface properties that can be modified during preparation and after processing [7]. Top-down processing methods include molecular beam epitaxy (MBE), electron lithography and X-ray lithography. Bottom-up methods include into wet-chemical and vapor-phase methods. Moreover, bottom-up methods also include hydrothermal methods consisting in the synthesis in an aqueous solution, at high temperature and under high pressure of steam[8-10]. The rapid development of nanomaterials synthesis techniques has brought many benefits in various fields of science and engineering, but also introduced several new problems. One of them is the synthesis of nanomaterials, which usually requires high energy consumption and the use of toxic chemical reagents. It is generally thought that synthesis methods increase production costs and aren’t environmentally friendly. Therefore, research is ongoing on the use of environmentally friendly and
renewable raw materials [11-12]. Through, hydrothermal carbonization method, carbon quantum dots can be obtained from any biomass. It is a cheap, eco friendly and non-toxic way to produce CQDs from many carbon precursors. Typically, the carbon precursor solution is sealed and reacts in a hydrothermal reactor at high temperature [9,13-14].

In this paper carbon quantum dots were synthesised with hydrothermal carbonization method from gelatin and a hypoallergenic milk for the babies. Gelatin and a hypoallergenic milk were used for the synthesis due to the high content of amino acids, which has a beneficial effect on the preparation of CQDs with high photoluminescence quantum yield. Toxic chemicals weren't used to obtain CQDs [15-20].

2. Experimental

The precursor of carbon to obtain carbon quantum dots was commercial gelatin, spirit vinegar (10% acidity) and a hypoallergenic milk. Sample 1 was prepared from 13.2g of gelatin dissolved in 40ml distilled water with the addition of 2.5ml spirit vinegar. Then the solution was poured into a stainless steel autoclave with a teflon liner and heated for 6h at 180℃. Figure 1 presents picture of autoclave. Subsequently, the autoclave was cooled to room temperature.

Figure 1. Autoclave with a teflon liner.

![Autoclave with teflon liner](image1.png)

Figure 2. Scheme of production and filtration.

![Scheme of production and filtration](image2.png)
The resulting solution was diluted three times, five times and ten times with distilled water. Sample 2 was prepared from 1g of gelatin dissolved in 40ml distilled water with the addition of 1ml spirit vinegar. Next, the solution was placed in an autoclave and heated for 3h at 200°C. Sample 3 was prepared and filtered similarly to Sample 2, without the addition of spirit vinegar. Sample 4 was prepared with 4.5g of hypoallergenic milk and 30ml of distilled water, then the solution was placed in an autoclave and heated for 3h at 180 °C. All the resulting solutions were ultrasonicated for 10min, centrifuged for 45min at 6000 rpm, washed with dichloromethane to remove the unreacted organic moieties and then filtered using PES filters. Figure 2 illustrated scheme of production and filtration solution of CQDs.

The UV-VIS Cary 100 Bio spectrophotometer from Varian and the Al-Prof SM1 Hm spectrometer were used to characterize the optical properties of carbon quantum dots.

3. Results and discussion
Using UV-VIS spectrophotometry, the maximum absorbance of carbon quantum dots obtained from food products was determined. The absorption spectrum for sample 1, diluted three times is illustrated in Figure 3.

![Figure 3](image)

**Figure 3.** UV–VIS absorption spectrum.

Figure 3 shows the UV - VIS spectrum for an aqueous CQDs solution obtained from gelatin, diluted three times. As shown in Figure 3, the absorbance spectrum shows a broad peak in the range of ~ 368nm to ~ 440nm, with a maximum at 408nm. Based on the range of absorbance spectra and its maximum values, it can be assumed that there was n–π* transition of CQO bonds or other connected groups in all samples.

![Figure 4](image)

**Figure 4.** Sample 1: (a) photoluminescence emission spectrum, (b) sample under UV light.
The maximum emission of CQDs was determined using the Al-Prof SM1 Hm spectrometer. The results are presented in Figure 4 for sample 1, diluted three times.

Figure 4 presents the photoluminescence spectrum of sample 1 diluted three times. The maximum emission of excited carbon quantum dots was ~558nm. Determination of the maximum corresponds to the wavelength for green emission.

4. Conclusions
Commercial gelatin and hypoallergenic milk for babies was used for the research. Based on the literature data, this food products were selected due to the high content of amino acids in the composition, which in turn affects the quantum yield and fluorescence properties of the obtained quantum carbon dots. Optical properties were tested using a UV - VIS spectrophotometer. All of the tested samples show broad absorbance peaks which may indicate molecular excitation in the wavelength range corresponding to ultraviolet and violet light. Based on UV-VIS spectra, it can be assumed that the concentration of the solution affects its optical properties. The excitation of the obtained carbon quantum dots was induced by a UV lamp emitting light in the range from 360 to 370 nm. All solutions were found to emit green light. Based on the UV-VIS spectrophotometric and spectrometric analysis and based on the literature data, it can be assumed that the obtained solutions contain carbon quantum dots. This article proves that it is possible to obtain CQDs from food products, cheap and environmentally friendly hydrothermal carbonization method. Toxic chemicals weren’t used to produce CQDs.

5. References
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