BŞEÜ Fen Bilimleri Dergisi
8(2), 924-930, 2021

BSEU Journal of Science
https://doi.org/10.35193/bseufbd.979306

e-ISSN: 2458-7575 (https://dergipark.org.tr/tr/pub/bseufbd)

Araştırma Makalesi -Research Article

Carbon Dots from Turnip Juice: Synthesis, Characterization and Investigation of pH-Dependent Optical Properties

Şalgam Suyundan Karbon Noktalar: Sentezi, Karakterizasyonu ve pH-Bağımlı Optic Özelliklerinin İncelenmesi

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Geliş / Received: 05/08/2021 ***Revize / Revised: 23/09/2021*** ***Kabul / Accepted: 27/09/2021***

ABSTRACT

In this study, carbon dots (CDs) were synthesized using a simple one-pot hydrothermal method by using turnip juice as carbon source. The water-soluble nontoxic carbon dots were obtained after reaction. The structural and optical properties of as synthesized CDs were elucidated by X-ray diffraction (XRD), Raman, Fourier Transmission Infrared (FTIR), UV–Vis absorption and Photoluminescence (PL) spectroscopy. A contour plot of the excitation dependent PL spectra of the turnip juice derived CDs and PL emission spectra in 3D color map were plotted. The maximum PL emission was found at 434 nm when excited at 364. The pH dependent luminescence properties of the CDs were investigated from pH 2-12 range in phosphate buffer solution (PBS). The resulting CDs can be evaluated in a variety of application areas, from anti-counterfeiting to bioimaging.

Keywords- Carbon Dots, Turnip Juice, Ph Dependent Photoluminescence

ÖZ

Bu çalışmada, karbon kaynağı olarak şalgam suyu kullanılarak basit ve tek aşamalı hidrotermal sentez yöntemi ile karbon noktalar (KN'lar) sentezlenmiştir. Reaksiyon sonrasında suda çözülebilen ve toksit olmayan karbon noktalar elde edilmiştir. Sentezlenen KN'ların yapısal karakterizasyonu ve optik özellikleri, X-ışını kırınımı (XRD), Raman, Fourier Dönüşümlü Kızılötesi spektroskopisi (FTIR), UV-Vis ve Fotolüminesans (FL) spektroskopisi ile aydınlatılmıştır. Şalgam suyundan elde edilen KN'ların FL spektrumlarının düzey çizgili grafiği ve 3D renkli harita yüzey görüntüsü çizildi. Maksimum FL emisyonu, 364 nm'de uyarıldığında, 434 nm'de bulunmuştur. CD'lerin pH'a bağlı lüminesans özellikleri, fosfat tampon çözeltisi kullanılarak pH 2-12 aralığından araştırılmıştır. Ortaya çıkan CD'ler, sahteciliğe karşı korumadan biyogörüntülemeye kadar çeşitli uygulama alanlarında değerlendirilebilir.

Anahtar Kelimeler- Karbon Noktalar, Şalgam Suyu, Ph Bağımlı Fotolüminesans

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I. INTRODUCTION

Carbon dots (CDs) are a special member of an important carbon nanomaterial family that has attracted attention in recent years. CDs are known as quasi-spherical particles with sizes below 10 nm. Studies on CDs are increasing day by day, and the application areas of carbon dots are expanding accordingly. These special nanoparticles have a place in many different application fields, such as bio-imaging, optical sensor, catalysis and solar cells because of unique photoluminescence (PL) properties, water solubility, chemical stability and low cost [1,2]. The most of the interest is given to PL properties of CDs, and they can exhibit both excitation dependent and excitation independent PL behaviour. Compared to quantum dots, CDs are superior in terms of non-toxic nature, synthesize procedure and synthesize cost; because of this reason, CDs are also considered as potential alternative to quantum dots [3,4].

The synthesis of CDs is divided into two categories namely top-down and bottom up [5]. At the top-down category, bulk carbon nanomaterials converted to tiny pieces. Laser ablation, arc discharge, electrochemical oxidation method are common example of this approach [6–8]. At the bottom up approach, carbon dots derived from small organic molecular precursors. Hydrothermal treatment, pyrolytic process, plasma treatment, microwave synthesis [9], chemical oxidation, and thermal decomposition are some common methods in this approach [10,11]. In bottom up approach, carbon dots can obtained from every carbonic material which can burn under suitable condition [12]. Finally, this method offer some advantages regarding to large scale CDs production and synthesis cost [3].

In the different application areas of CDs sensitivity, pH is very important. For instance, intracellular pH is important for the functions of organelles and metabolism of the cells [8]. In literature, pH dependent PL properties of CDs have been examined by different works. The linear relationship of PL intensity of the ascorbic acid derived CDs between pH 4 to pH 8 was found b Jia et al. [13]. Ghanem et al, synthesized N-doped CDs and investigate pH dependent PL properties of the CDs. A linear relationship of pH dependent PL values between pH 1 to pH 7 was obtained [14]. The PL intensity of CDs from pH 2 to pH 12 was investigated and possibility of optical pH sensors was discussed by Zhang et al [15]. The PL peak position slightly change between pH 2 to pH 6 and from pH 7 to pH 12 redshift of PL peak position from 458 nm to 491 nm was found at the mentioned study. To sum up, pH dependent PL properties of the CDs discussed in previous studies but the of linear pH ranges is need to investigate more. Since the synthesis of CDs that PL behaviour shows long rang linear response to pH is important for optical sensors.

Turnip juice is known as traditional Turkish beverage. It contains black carrots, bulgur flour, turnip, Baker's yeast and rock salt. This beverage is purplish-red color due to black carrot content [16]. It is produced by lactic acid fermentation. Generally this beverage manufactured in Adana, Mersin, Kahramanmaraş, Gaziantep, Osmaniye and Hatay provinces in Turkey [17]. In this study, turnip juice was chosen as a carbon source due to its rich components, such as β-carotene, group B vitamins, calcium, potassium, and iron [18]. The present study, to best of our knowledge for the first-time turnip juice was used to synthesis CDs by hydrothermal method. The synthesized CDs were characterized and pH-dependent optical properties were investigated.

II. MATERIALS AND METHODS

A. Synthesis of the C-Dots

The CDs were synthesized by a simple, one-pot and fast hydrothermal method. Turnip juice was obtained from local market. Shortly, 50 ml turnip juice was placed into teflon-lined stainless steel autclave for 10h at 180 ºC. After the carbonization process, the product was cooled to room temperature naturally, and the brownish solution product was filtered. After that, the filtered solution mixture placed in the falcon tubes was centrifuged at 15000 rpm for 20 minutes to allow the large particles to settle to the bottom. The obtained CD samples were kept in the fridge at 4 °C for experimentation and characterization processes that would be carried out in later stages.

B. Apparatus and Reagents

Optical properties of the sythesized CDs were examined by using UV–Vis absorption spectra (Shimadzu-1800 UV–Vis spectrometer) and Photoluminescence (PL) spectrum (Varian Cary Eclipse spectrometer) respectively. The excitation/emission slit width was adjusted as 5/20 nm. Crysatlline pattern of CDs were measured by XRD instrument with Philips X`Pert PRO XRD with Cu Kα radiation (λ = 0.154056 nm, set at 40 kV and 30

mA). Raman spectrum of synthesized CDs was explored with a portable Raman spectrometer BWS465 B&W Tek Inc (an excitation wavelength of 785 nm). Fourier Transmission Infrared spectroscopy (FTIR) was examined out on a Perkin Elmer Spectrum 400 with a universal demountable cell mount for liquid samples in the range of 4000 to 400 cm $^{-1}$. The pH meters Thermo Scientific A215 were used for the pH measurements. Dynamica Velocity centrifuge was used to separete larger carbon nanoparticles . All chemicals were of analytical grade, and fresh distilled and deionized water was used to prepare all solutions.

III. RESULTS AND DISCUSSION

The X-ray diffractograms of the synthesized CDs is demonstrated in Figure 1. There is broad diffraction peak at 24.01º that is corresponding to graphitic structure. Moreover, the wide diffraction peak is attributed to small size of synthesized CDs [15]. This apparent peak corresponds to (002) plane and the interlayer spacing was calculated as 0.37 nm. The wide diffraction peak also related to amorphous nature of synthesized carbon dots [19,20]. Raman spectrum was also measured to underline structural properties of the CDs and it is given in Figure 2. The two clear peak at 1344 and 1538 cm^{-1} in the spectrum is shown that is attributed to D-band (sp^3 defects) and G-band (sp^2 clusters) respectively [21,22].

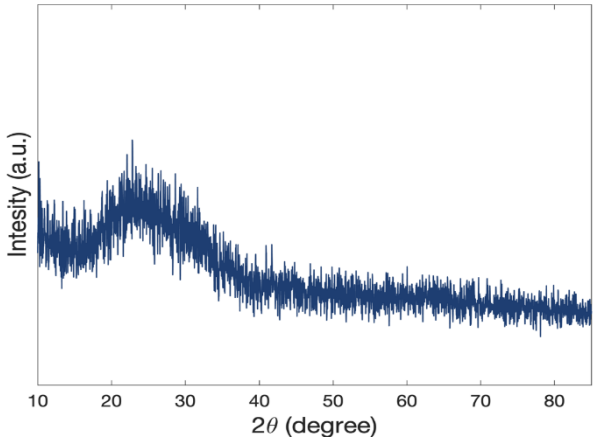

Figure 1. XRD pattern of the synthesized CDs.

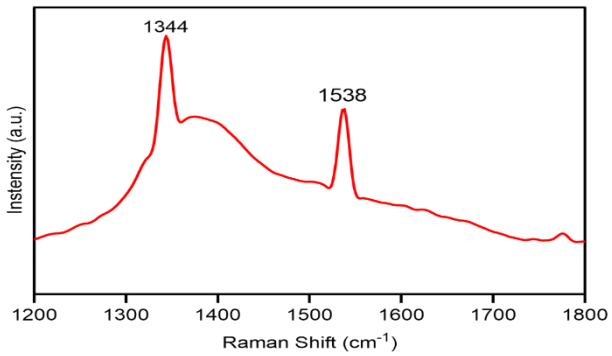

Figure 2. Raman spectrum of the prepared CDs.

The UV-Vis spectrum of turnip juice derived carbon dots is demonstrated in Figure 3. As shown in this figure, the synthesized CDs gives a strong absorption peak at 280 nm which is attributed to π-π* transition of the C=C bonds of the aromatic rings [23]. Also the long tail to 600 nm indicate to occurrence of CDs [24]. Infrared spectroscopy of carbon dots was taken to further prove the presence of important functional groups in the structure of the CDs. As seen in Figure 4, infrared spectrum of turnip CDs, O-H vibration stretching and C=O vibration stretching peaks were observed, respectively, at 3438 and 1636 cm^{-1}. There is a small peak between these two main CDs peaks which shown in 2183 cm^{-1} is attributed C≡C vibration stretching [7]. In the light of this spectrum of CDs, the existence of these functional groups, such as -OH, -COOH and benzene ring can be evaluated in advance. These two stretching peaks are particularly important evidence of the presence of the sp^2 hybrid honeycomb cage in the structure of the CDs [25].

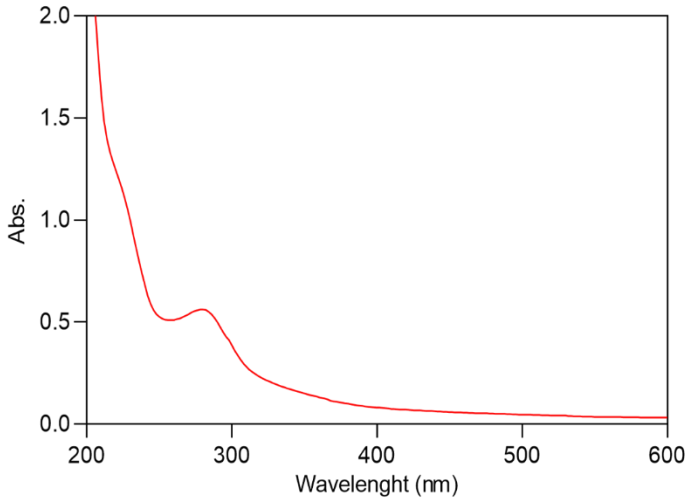

Figure 3. UV-Vis spectrum of the turnip juice derived CDs.

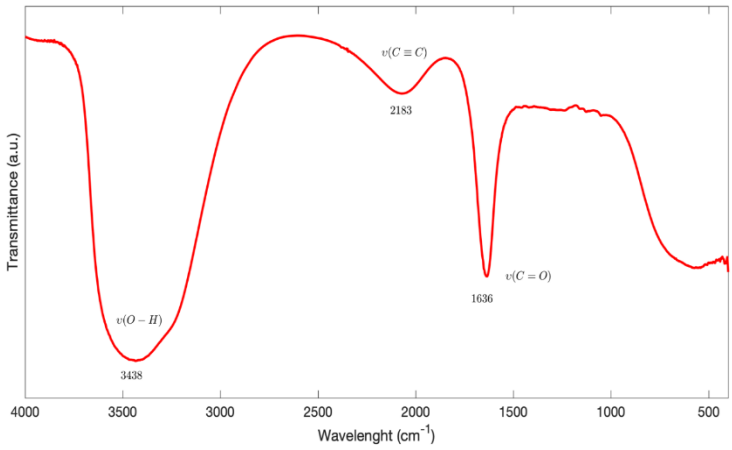

Figure 4. FTIR spectrum of the synthesized CDs.

The excitation dependent photoluminescence (PL) properties of the hydrothermally synthesized CDs is illustrated in Figure 5. As the excitation wavelength increase, the intensity of emission peak also increases and reached the maximum value of 434 nm when excited at 364 nm, but after this point, emission peak decreases in the PL intensity. The excitation wavelength were ranging from 336 nm to 436 nm, and the redshift in the emission intensity were found with increasing excitation wavelength and after emission peak stats to decrease after certain point that is refer to common feature of the formation of CDs [26]. The existences of different surface active states on CD might the reason of excitation dependent PL properties of the synthesized CDs [23,27].

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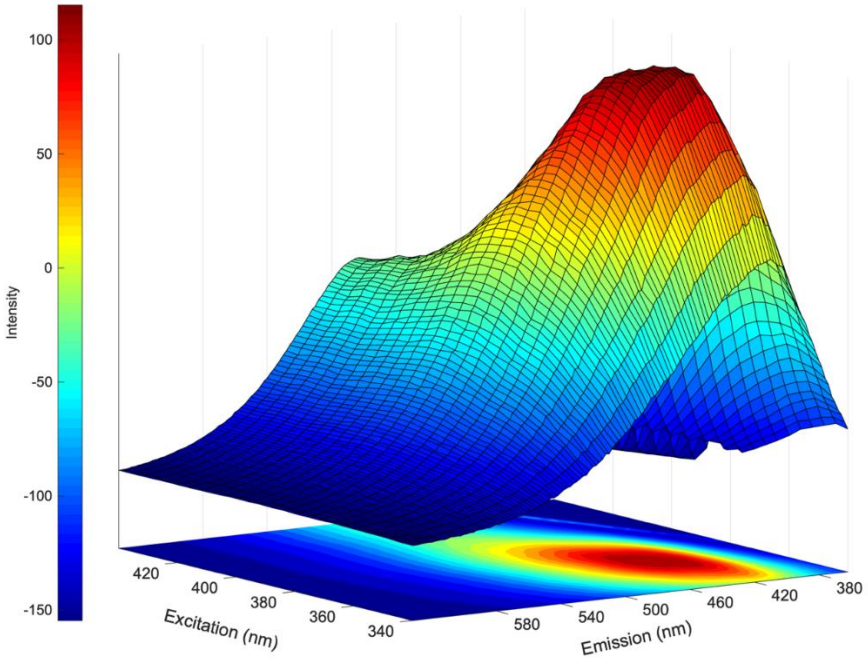

Figure 5. A contour plot of the excitation dependent PL spectra of the turnip juice derived CDs and 3D PL excitation emission map.

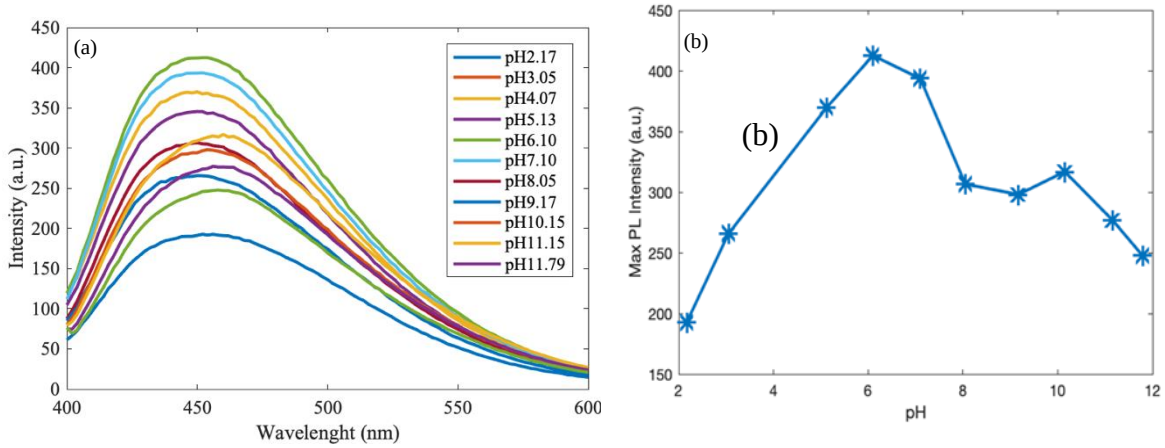

Figure 6. (a) The turnip juice derived CDs pH dependent P emission spectra, (b) The maximum emission peak versus pH values.

It is important to examine the relationship of fluorescence behaviour of carbon dots with pH change. Accordingly, since the pH stability in carbon dots applications can directly affect the spectral properties of carbon dots, it is worth researching how it will change in acidic, basic, and neutral media. In this context, the impact of pH values on PL emission intensity of turnip juice derived carbon dots was investigated. The prepared carbon dots were dispersed in pure water. The pH measurements were taken with phosphate buffer solution (PBS) within pH range of 2 to 12 and the spectra were demonstrated in Figure 6 (a) and (b). Figure 6 (a) illustrate the emission spectra of the CDs as a function of pH at 364_{ex}. As seen from the Figure 6 (b), the behaviour of pH dependent PL may be investigated in four main regions. Firstly, in acidic medium; the emission intensity was gradually increased from pH 2 to pH 6. The max PL intensity of turnip juice derived CDs was found at pH 6. At the second region, from the pH 6 to 8 the intensity of PL peak sharply decreased. This may be due to protonation or deprotonation of groups, such as C=O, OH, -COOH on CDs surface in acidic and basic environments [26]. However, as the media more basic (from pH 8-to 10) the PL intensity mostly stable (third region). At the last region, PL intensity also decreases with the increase of basicity.

IV. CONCLUSION

Herein we report, turnip juice derived carbon dots by hydrothermal method without any chemical regents. The as prepared CDs were characterized by several analytical and instrumental techniques, such as XRD, FTIR, Raman, Uv-vis, PL spectroscopy. The XRD results revealed that the synthesized CDs were amorphous nature. The maximum emission of CDs was found at 434 nm when excited at 364 nm. The pH dependent luminescence properties of the CDs were investigated wide pH range in PBS. According pH dependent PL results, the maximum intensity of luminescence peak was strongly related to pH values of media. The main reason of this phenomena protonation or deprotonation of groups, such as C=O, OH, -COOH on CDs surface in acidic and basic environments. The prepared CDs would be used in different application areas.

ACKNOWLEDGMENTS

This work was financially supported by the Kahramanmaraş Sütçü İmam University Scientific Research Projects Coordination Unit (Project Number: 2019/5-21 M and 2021/1-7 YLS).

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