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SYNTHESIS OF FLUORESCENT CARBON QUANTUM DOTS WITH HYDROTHERMAL AND SOLVOTHERMAL METHOD APPLICATION FOR ANTICOUNTERFEITING AND ENCRYPTION

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Abstract

Original scientific paper

The objective of this work was to compare the optical performance of hydrothermally and solvothermal synthesized unique fluorescent carbon quantum dots (FCQDs) from organic material and use it as a fluorescent ink for one of the significant information encryption applications. The goji berry and sucrose were used as carbon sources for the experiment. FCQDs are obtained by simple hydrothermal and solvothermal methods using water, isopropanol and acetone as a solvent. The crystal structure and optical properties of the obtained carbon dots are investigated. All obtained FCQDs are amorphous phases. The maximum emission of the obtained FCQDs was found at 465 nm when excited at 386 nm. Among the carbon dot samples synthesized using three different solvents, the sample with the highest PL peak value was found in the sample synthesized with acetone solvent. The morphology of the carbon dot sample produced with acetone solution was examined by TEM and the average diameter of the carbon dots was calculated as 7.2 nm. The fluorescent ink potential of the synthesized FCQDs was compared and the best result found at the carbon dot that was synthesized from solvothermal methods with an acetone solution.

Keywords: *Carbon dots; fluorescence ink; goji berry; information encryption; XRD.*

SAHTECİLİKLE MÜCADELE VE ŞİFRELEME UYGULAMASI İÇİN HİDROTERMAL VE SOLVOTERMAL YÖNTEM İLE FLUORESAN KARBON KUANTUM NOKTALARININ SENTEZİ

Özet

Orijinal bilimsel makale

Bu çalışmanın amacı, organik bir malzemeden hidrotermal ve solvotermal yöntemle sentezlenen floresan karbon kuantum noktalarının (FCQDs) optik performanslarını karşılaştırmak ve bunları önemli bilgi şifreleme uygulamalarından biri için bir floresan mürekkep olarak kullanmaktır. Goji berry ve sakkaroz, çalışmada karbon kaynağı olarak kullanılmıştır. FCQD'ler, çözücü olarak su, izopropanol ve aseton kullanılarak hidrotermal ve solvotermal yöntemlerle elde edildi. Elde edilen karbon noktalarının kristal yapıları ve optiksel özellikleri araştırılmıştır. Elde edilen bütün FCQD'ler amorf fazdadır. FQCD'ler 386 nm'de uyarıldığında maksimum emisyonu 465 nm'de elde edilmiştir. Üç farklı çözücü kullanılarak sentezlenen karbon nokta örnekleri arasında en yüksek PL pik değeri aseton çözücü ile sentezlenen örnekte bulunmuştur. Aseton solüsyonu ile üretilen karbon nokta örneğinin morfolojisi TEM ile incelenmiş ve karbon noktaların ortalama çapı 7,2 nm olarak hesaplanmıştır. Sentezlenmiş FCQD'lerin floresan mürekkep olarak kullanılabilme potansiyeli karşılaştırılmış ve en iyi sonuç aseton çözücüsünde solvotermal yöntemle sentezlenen karbon noktaları için bulunmuştur.

Anahtar Kelimeler: *Karbon noktası; bilgi şifreleme; Floresans mürekkep; goji beri; XRD.*

1 Introduction

Today, with the growth in scientific studies, there has been a significant increase in the development of new materials with superior properties. Among them, nanostructured materials are known as one of the most researched and studied groups. Although there are various types of nanostructured materials, carbon based nanostructured materials have attracted specific interest. The newest members of carbon nanostructures are called CDs (carbon dots) or CQDs (carbon quantum dots). Carbon dots were found by chance in 2004 during the purification of carbon nanotubes and were subsequently obtained using laser ablation of graphite [1,2]. After this

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discovery, the attractive, impressive, superior and unique properties of carbon dots were revealed and a new era began in terms of engineering science [3].

The size of the carbon dots is 10 nm or less. They have superior fluorescence properties in terms of their characteristics [4]. Carbon dots have superior fluorescence and optical properties as well as biocompatibility. Moreover, they have easy synthesis routes and pollution free precursors. Carbon dots, which have been studied by many scientists in recent years, have been found to have a number of exciting properties [5]. Carbon dots find a place in the theoretical and application areas in many fields such as science, engineering and health, thanks to their strength, optical, mechanical and electrical properties [6–8]. The most important feature of carbon dots is surface functionality that exhibits strong PL (photoluminescence), according to their size and excitation wavelength [6]. In addition to these properties, it is very valuable for its excellent biocompatibility, water solubility, low cost, low toxicity, easy synthesis, photostability and chemical stability. Considering these advantages, it has applications in many fields, such as bioimaging, sensor, solar cells, photocatalysis and drug delivery [9]. Carbon dots can be obtained from many natural sources such as food, waste and nutrients with the advantage of low cost [10].

Different organic sources have been used as carbon precursors for CD synthesis. For example, tangerine juice/onion Shell [11] turnip juice [12], rosemary leaves [13], pigeon manure [14], cowberry [15], blueberry [16], blackberry and raspberry [17]. The most known name of the goji berry is "wolfberry". This name is based on the root "gou" meaning wolf [18]. The name goji is derived from several local words and was first coined by TBRI (Tanaduk Botanical Research Institute) researchers in 1973 [19]. Goji Berry, Latin name Lycium barbarum, is a shrub of the Solanaceae family from Southeast Asia and grows in China, Tibet and other parts of Asia. Its fruits are 1-2 cm long. It is bright red in color and elliptical in shape [20,21]. Goji Berry fruit is highly nutritious. It has become more popular in the last few years due to its recognition as a "superfood" among people.

Due to its nutritional value, it has become more preferred by people today. The fruit contains sugar [19]. Goji berry has several important biological functions, such as boosting immunity, anti-aging, anti-tumor and antioxidant [18]. Digital security is crucial in the information era because counterfeiting not only results in significant economic losses but also has negative effects on people's physical and mental health. Luminescent inks have drawn a lot of interest among the many anti-counterfeiting substances due to their numerous uses in information coding, information storage, and information security. A significant barrier still exists in the production of high anti-counterfeiting strategies and aqueous luminous anti-counterfeiting nanomaterials [22–25].

Sucrose was also added to the goji berry to strengthen the PL peaks of the synthesized carbon spots, based on a related work in the literature [26,27]. Precursors, synthesis procedures, particle size, fundamental PL characteristics, applications, and findings from this work are summarized in Table 1. In this study, goji berry (Lycium barbarum) was used as a natural carbon source. CDs were synthesized by hydrothermal and solvothermal methods. While synthesizing carbon dots, acetone, ultrapure water and isopropyl alcohol were used as solvents, and carbon dot samples synthesized using this solvent were compared. The structural properties of carbon dots were researched by XRD analysis. In addition, the optical properties of the synthesized materials were investigated in UV-Vis spectroscopy. The photoluminescence properties of the obtained nanoparticles with carbon dots were researched by photoluminescence spectrometry. FTIR spectrometer was used to analyze its chemical structure.

Table 1. Carbon source, size, PL properties and application examples used in preparing carbon dots.

Carbon precursors	Synthesis methods	Size (nm)	PL features	Application	Reference
Tea residue/ Choline chloride/ Urea	Hydrothermal	< 10	Ex: 330 nm Em: 410 nm	Sensing	[28]
Chia seed	Hydrothermal	5.4	Ex: 310 nm Em: 415 nm	Cell imaging	[29]
Aconitic acid/ PEI	Thermal carbonization	11.12	Ex: 440 nm Em: 485 nm	Sensing	[30]
Citric Acid/ m-PD	Hydrothermal	3.03 to 3.73	Ex: 320 nm Em: 466 nm	Information encryption, Anti-Counterfeiting	[31]
Laurus nobilis leaves	Hydrothermal	< 10	Ex: 344 nm Em: 425 nm	Fluorescent ink	[32]
Waste corn husk	Hydrothermal	5.39	Ex: 342 nm Em: 428 nm	Composite material	[33]
Rosemary leaves	Hydrothermal	16.13	Ex: 332 nm Em: 422 nm	Food storage, fingerprint detection, antibacterial activity	[13]
Citric Acid/ PEI	Microwave-assisted	12	Ex: 354 nm Em: 442 nm	TNT determination	[34]
Citric Acid	Microwave-assisted	3		Fish gelatin films	[35]
Cowberry	Hydrothermal		Ex: 350 nm Em ~ 440 nm	Composite material	[15]
Blueberry	Facile liquid N_2 treatment method		Ex: 340 nm Em: 450 nm	Sensing	[16]
Goji berry	Hydrothermal Solvothermal	7.2	Ex: 386 nm Em: 465 nm	Information encryption, Anti-Counterfeiting	This work

2 Materials and Methods

2.1 Material

Goji berry was obtained in the personal garden of the author Hacı Veli Kalmış. Solvents purchased from standard manufacturers were used in the experiments. The ultrapure water used in the experiments was supplied from the KSÜ ÜSKİM unit. All materials were used in their current form without purification.

2.2 Preparation of CD Nanoparticles

Goji berry was chosen as a natural carbon source. Goji beryy was cleaned by washing with tap water. It was then washed with pure water. Then, the goji berry was kept in an oven at 60°C for 96 hours to be dried. The dried goji berry was sieved after grinding. 1.25 g of goji berry powder and 1.25 g of sucrose were mixed in 150 ml of solvent in an ultrasonic treatment. Ultrapure water, acetone and isopropyl alcohol were used as solvents. The carbon dots were synthesized using three different solvents. The homogenized mixture was transferred to a teflon box. The Teflon box was then placed in an autoclave made of stainless steel. After being placed in the autoclave oven, it was subjected to hydrothermal and solvothermal treatment at 175°C for 8 hours. At the end of the process, the autoclave was taken from the oven to cool itself to room temperature. The resulting solution was filtered. It was centrifuged and dried. It was stored at 4 °C for experiments. The final concentration of the carbon dots in solution for measurements was 0.25 mg mL^{-1}. The schematic representation of the experimental setup is given in Figure 1. While synthesizing carbon dots, acetone, ultrapure water and isopropyl alcohol were used as solvents, and carbon dot samples synthesized using this solvent were named as GCDa, GCDw and GCDi, respectively.

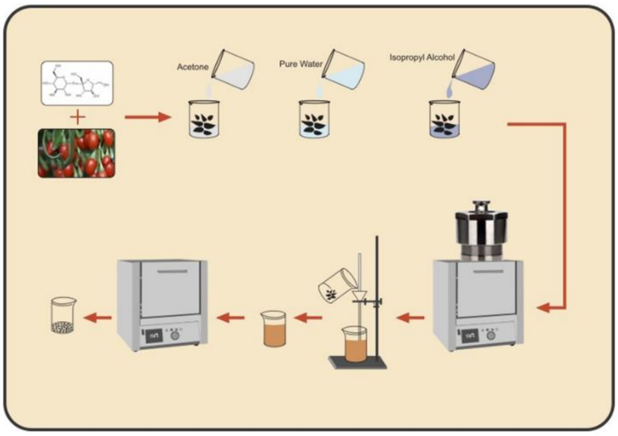

Figure 1. Symbolic representation of obtaining carbon dots from Goji berry.

2.3 Characterization

Structural characterization of the synthesized Carbon dots samples was examined by XRD (X-ray diffraction). Philips X'Pert PRO XRD device with Cu Kα radiation (λ = 0,154056 nm, tuned at 40 kV and 30 mA) was used to detect the XRD pattern. The optical properties of the synthesized carbon dot samples were obtained by UV-Visible Spectrophotometer (Shimadzu UV 1800) at room temperature. FTIR Spectroscopy: Measured with a Perkin Elmer Spectrum 400 instrument in the 4000–450 cm^{-1} range. The PL spectra of the CD samples were scanned with the Varian Cary Eclipse spectrometer.

3 Results and Discussion

The XRD pattern showing the crystal structures of the carbon dots synthesized from Goji berry is presented in Figure 2. CDs synthesized in the XRD plot appear to have flat amorphous peaks similar to the structure of 2θ=23˚ graphene. Pure graphite has a significant peak at 2θ=26.42° that corresponds to the (002) plane in the X-ray pattern, while GO has two distinctive peaks at 2θ=11° and 2θ=42° that correlate to the (001) and (100) planes [36]. For multi-walled carbon nanotubes, two diffraction peaks with centers at 26° and 45° are often seen. These peaks are designated as (002) and (001) planes [37]. Generally, amorphous carbons with graphitic domains are indicative of carbonaceous materials (sp2 domains). The two broad Bragg peaks at 22.0 and 43.7 were indexed to the graphite hexagonal structure's (002) and (100) planes, respectively [38]. This broad and amorphous peak has also been detected in XRD plots of CDs in many studies [32,39,40].

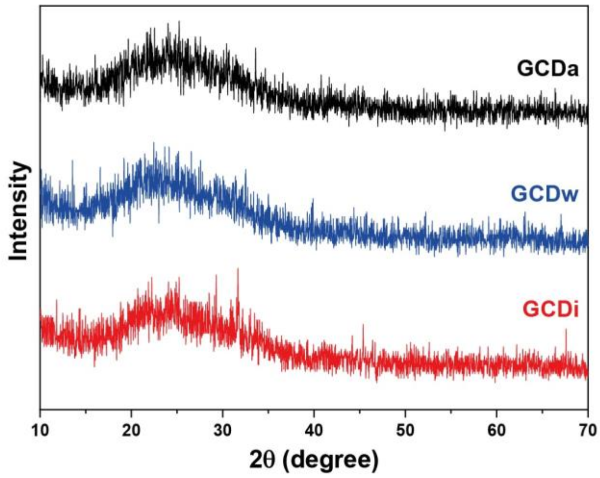

Figure 2 XRD pattern of CDs

UV-Visible spectroscopy can be used to observe what changes nanoparticles undergo as time passes. Carbon nanoparticles can be characterized by UV-Visible spectroscopy [41]. Carbon dots synthesized from Goji berry were examined by UV-Visible spectroscopy. The UV-Visible absorption graph is given in Figure 3. A sharp absorption peak similar to a π-π* transition was seen in the UV–Visible spectrum at 282 nm [42]. Figure 4a illustrates PL spectra of the obtained carbon dots in different solvents and when the samples are excited at 386 nm wavelength, they exhibit maximum emission at 465 nm (Figure 4b). The maximum PL intensity was found in the carbon dots sample which is dissolved in acetone. Photoluminescence spectra of carbon dot sample (GCDa) dissolved in water were investigated using PL spectrometry by varying the wavelength between 400-600 nm (Figure 5). It was observed that the synthesized CD samples gave excitation-induced emission. When the excitation wavelength was changed from 386 nm to 456 nm with 5 nm intervals, the emission peak was redshifted from 465 nm to 508 nm. The observed redshift in the emission spectrum indicates the possibility of tunability of the PL emission color. Depending on the increase in the excitation wavelength, the intensity of the fluorescence peak decreases and exhibits attenuation [33]. This result is due to electron and hole recombination produced on the surface of CDs. The redshift observed with the difference in excitation wavelengths can be attributed to the difference in the surface sizes of the CDs [42].

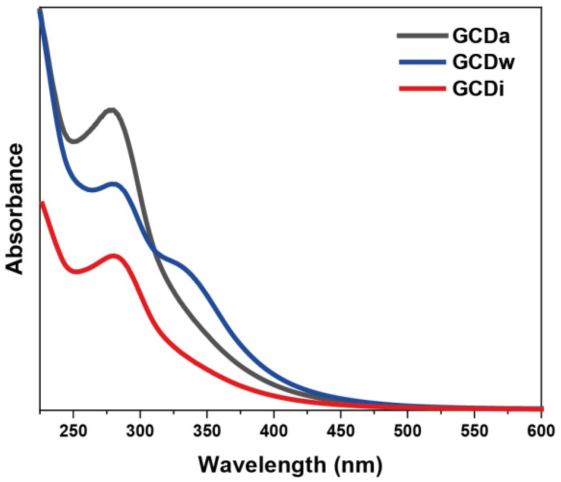

Figure 3. UV-Vis spectrum of synthesized carbon dots from Goji berry.

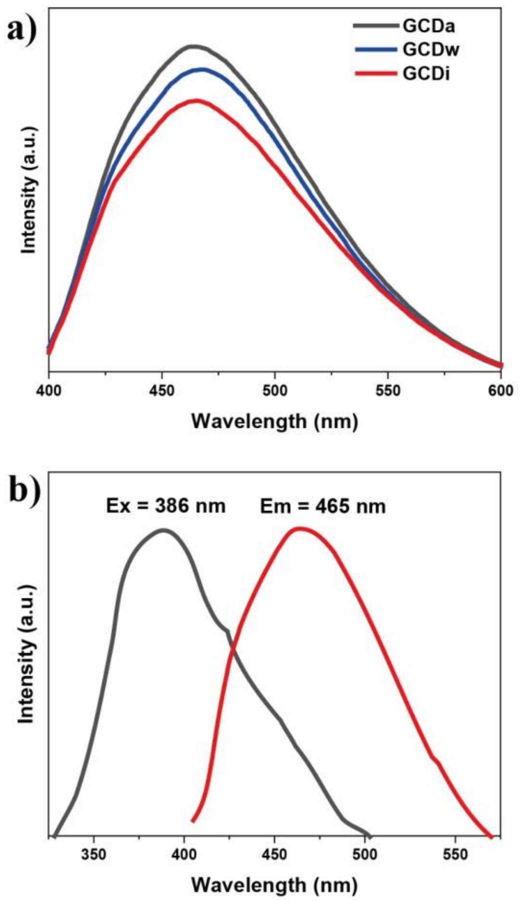

Figure 4. a) PL spectra of CDs synthesized in different solvents b) Excitation and emission spectrum of product GCDa.

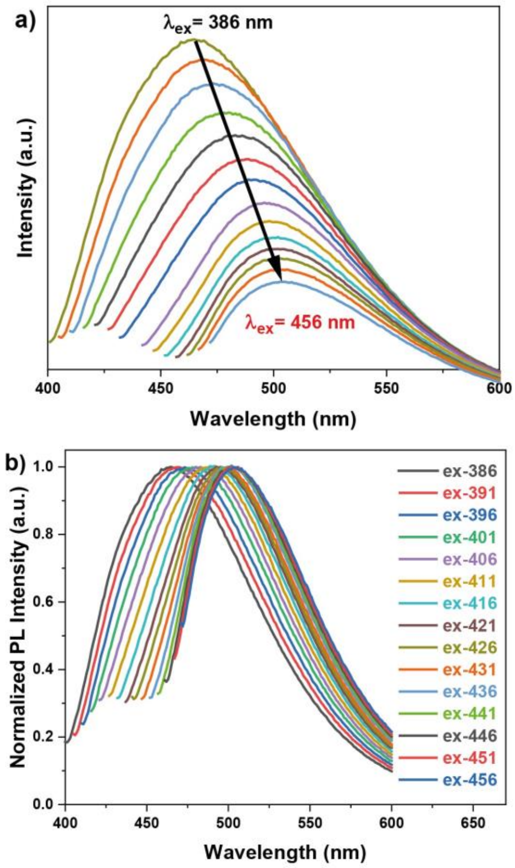

Figure 5. a) Excitation dependent PL spectra of GCDa, b) after normalization.

FTIR measurements were taken in the 450-4000 cm^{-1} range to examine the chemical structure of the synthesized samples. FTIR results are presented in Figure 6. The broad peak seen at 3324 cm^{-1} is attributable to O–H or N–H stretching vibrations [43]. The absorbance peak of the samples at 2924 cm^{-1} and 2846 cm^{-1} coincides with the C–H bonds [44–46]. The 1706–1605 cm^{-1} double peak can be attributed to the stretching vibrations of the C–N and C–O bonds, respectively [44]. The C-N bonds observed in the FTIR analysis may be due to the amino groups in the proteins found in the structure of the goji berry [47]. The peaks of stretching vibration of the C–C, C–N, and C–O groups can be seen at 1372 cm^{-1}, 1200 cm^{-1} and 1100 cm^{-1}, respectively [48].

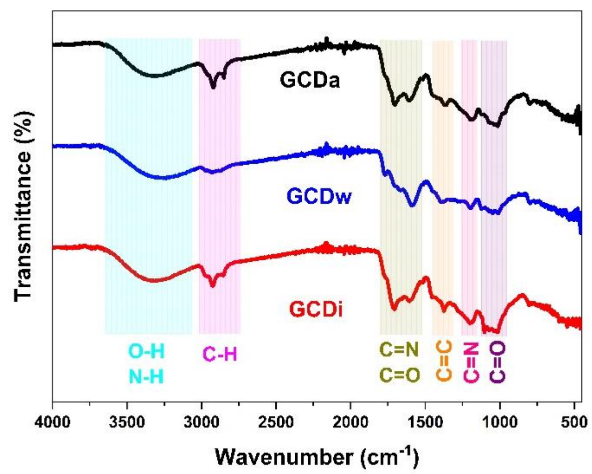

Figure 6. FT-IR spectrum of the CDs.

The morphological properties of synthesized CDs were studied, and Figure 7 depicts the form and size distribution of the carbon dots sample produced in acetone solution. GCDa sampe have homogeneous size and distribution, as observed in the TEM picture. The average diameter of the studied carbon dots was calculated to be 7.2 nm.

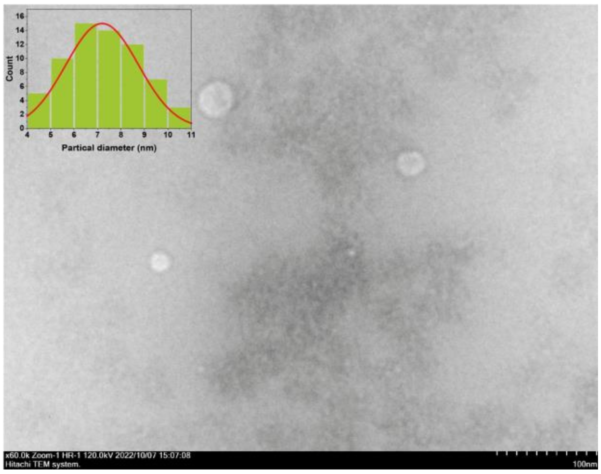

Figure 7. TEM image of GCDa sample.

Carbon dot samples were dissolved in distilled water. Then the carbon dots were centrifuged to separate large particles. The fluorescent abilities of the CDs obtained in Figure 8 are observed at a distance of 10-15 cm under UV light (365 nm). Under UV light, GCDa and GCDw carbon dot samples glowed turquoise. When the synthesized samples were compared, it was observed that the fluorescence irradiation was ordered as PGDa > PGDw > PGDi [14].

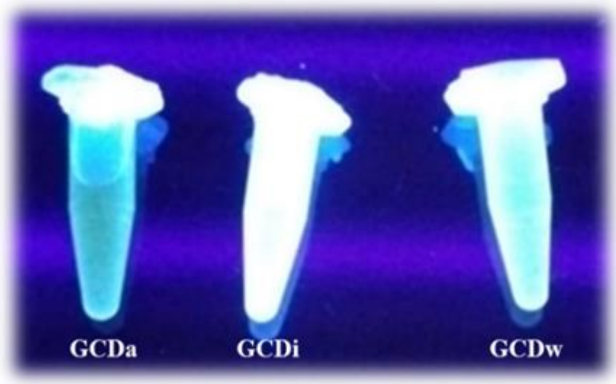

Figure 8. Image of GCDa, GCDi and GCDw samples under UV light, respectively.

CQDs are materials with serious potential as fluorescent inks that can be used in various applications due to their non-toxicity, fluorescent stability and similar properties. Fluorescent inks obtained using CQDs are environmentally friendly and permanent. Additionally, such fluorescent inks can be used in anti-fraud and encryption applications [14]. Interestingly, some luminescent materials with exceptional invisible transparency capabilities may be used spontaneously as luminescent inks (Figure 8). A brush and commercial papers without any background luminescence were used. The similar pattern may be readily obtained, as shown in Figure 9, by utilizing obtained GCDa, GCDw, and GCDi labeled carbon dots as luminous inks. This pattern was invisible in the daylight but was immediately visible under UV light. The best outcome for the GCDa carbon dot sample was produced, and it may be utilized as direct anti-counterfeiting luminescent inks. Utilizing carbon dots with a higher PL peak intensity can help luminescent inks' anti-counterfeiting capabilities.

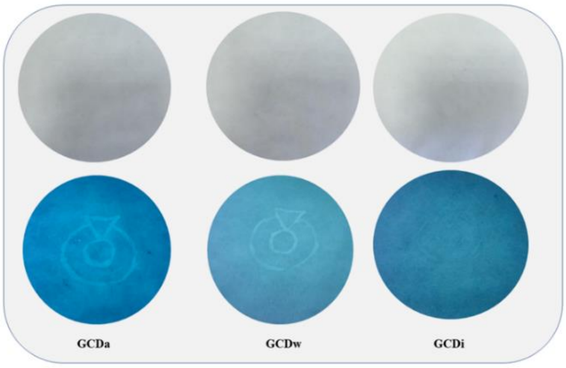

Figure 9. Images drawn with fluorescent ink created from CQDs in daylight and under UV light (365 nm).

4 Conclusion

Fluorescent carbon dots were synthesized from Goji berry simply, non-toxic, environmentally friendly and cost-effective. CDs were obtained by the hydrothermal and solvothermal methods using Goji berry and sucrose as a precursors and water, isopropanol and acetone as a solvent. The crystal structures of carbon quantum dots synthesized using different solvents were investigated by XRD and the crystal structure of obtained carbon dots consists of amorphous phases. The obtained peaks in the UV spectrum of carbon dots are attributed to π–π* electronic transitions. As a result of the excitation of the samples at a wavelength of 386 nm, it was observed that they exhibited maximum emission at a wavelength of 465 nm. By increasing the excitation wavelength, a redshift of the emission peak was detected. The sample with the highest PL peak value among the carbon dot samples generated using three different solvents was discovered in the sample synthesized using acetone solvent. TEM was used to study the morphology of the carbon dot sample synthesized with acetone solution, and the average diameter of the carbon dots was determined to be 7.2 nm. Obtained GCDa, GCDw, and GCDi carbon dots was utilized as luminous inks. This pattern was invisible in the daylight but was immediately visible under UV light. The best outcome for the GCDa carbon dot sample was produced, and it may be utilized as direct anti-counterfeiting luminescent inks.

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Declaration

Ethics committee approval is not required.

References

[1] Xu, X., Ray, R., Gu, Y., Ploehn, H.J., Gearheart, L., Raker, K., & Scrivens, W.A. (2004). Electrophoretic analysis and purification of fluorescent single-walled carbon nanotube fragments. *Journal of the American Chemical Society*, 126(40), 12736–12737.

[2] Sun, Y.P., Zhou, B., Lin, Y., Wang, W., Fernando, K.A.S., Pathak, P., et al. (2006). Quantum-sized carbon dots for bright and colorful photoluminescence. *Journal of the American Chemical Society*, 128(24), 7756–7757.

[3] Bhartiya, P., Singh, A., Kumar, H., Jain, T., Singh, B.K., & Dutta, P.K. (2016). Carbon dots: Chemistry, properties and applications. *Journal of the Indian Chemical Society*, 93(7), 759–766.

[4] Zhang, J. & Yu, S.H. (2016). Carbon dots: large-scale synthesis, sensing and bioimaging. *Materials Today*, 19 (7), 382–393.

[5] Wang, T., Wang, A., Wang, R., Liu, Z., Sun, Y., Shan, G., Chen, Y., & Liu.Y. (2019). Carbon dots with molecular fluorescence and their application as a "turn-off" fluorescent probe for ferricyanide detection. *Scientific Reports*, 9(1), 1–9.

[6] Wang, Y. & Hu, A. (2014). Carbon quantum dots: Synthesis, properties and applications. *Journal of Materials Chemistry C*, 2(34), 6921–6939.

[7] Xu, Y., Liu, J., Gao, C., & Wang, E. (2014). Applications of carbon quantum dots in electrochemiluminescence: A mini review. *Electrochemistry Communications*, 48, 151–154.

[8] Ibrayev, N., Dzhanabekova, R., Seliverstova, E., & Amanzholova, G. (2022). Optical properties of N- and S-doped carbon dots based on citric acid and L-cysteine. *Fullerenes, Nanotubes and Carbon Nanostructures,* 30(1), 22–26.

[9] Dinc, S. & Kara, M. (2018). Synthesis and Applications of Carbon Dots from Food and Natural Products. *Journal of Apitherapy and Nature/Apiterapi ve Doğa Dergisi,* 1(1), 33–37.

[10] Bag, P., Maurya, R. K., Dadwal, A., Sarkar, M., Chawla, P. A., Narang, R. K., & Kumar, B. (2021). Recent Development in Synthesis of Carbon Dots from Natural Resources and Their Applications in Biomedicine and Multi-Sensing Platform. *ChemistrySelect*, 6(11), 2774–2789.

[11] Başkaya, S.K. & Çeşme, M. (2021). Synthesis of N-Doped Carbon Quantum Dots by Hydrothermal Synthesis Method and Investigation of Optical Properties. *Türk Doğa ve Fen Dergisi*, 10(2), 206–211.

[12] Eskalen, H. & Çeşme, M. (2021). Carbon Dots from Turnip Juice: Synthesis, Characterization and Investigation of pH-Dependent Optical Properties. *Bilecik Seyh Edebali University Journal of Science*, 8(2), 924–930.

[13] Eskalen, H., Çeşme, M., Kerli, S., & Özğan, Ş. (2021). Green synthesis of water-soluble fluorescent carbon dots from rosemary leaves: Applications in food storage capacity, fingerprint detection, and antibacterial activity. *Journal of Chemical Research*, 45(5-6), 428–435.

[14] Başkaya, K., Tahta, B., Uruş, S., Eskalen, H., Çeşme, M., & Özğan, Ş. (2022). Multifunctional B, N, P, and S-doped fluorescent carbon quantum dot synthesis from pigeon manure: highly effective Hg (II) sensor and fluorescent ink properties. *Biomass Conversion and Biorefinery,* 1, 1–15.

[15] Kapitonov, A. N., Egorova, M. N., Tomskaya, A. E., Smagulova, S. A., & Alekseev, A. A. (2018). Hydrothermal synthesis of carbon dots and their luminescence. *AIP Conference Proceedings,* 2041(1), 030003.

[16] Aslandaş, A. M., Balci, N., Arik, M., Şakiroglu, H., Onganer, Y., & Meral, K. (2015). Liquid nitrogen-assisted synthesis of fluorescent carbon dots from Blueberry and their performance in Fe^{3+} detection. *Applied Surface Science*, 356, 747–752.

[17] Yang, Z., Xu, M., Wang, T., Wei, H., & Zhang, Y. (2015). Method for hydro-thermal synthesis of carbon quantum dots based on fruits, CN105366659A.

[18] Potterat, O. (2010). Goji (Lycium barbarum and L. chinense): Phytochemistry, pharmacology and safety in the perspective of traditional uses and recent popularity. *Planta Medica,* 76(1), 7–19.

[19] Amagase, H. & Farnsworth, N. R. (2011). A review of botanical characteristics, phytochemistry, clinical relevance in efficacy and safety of Lycium barbarum fruit (Goji). *Food Research International*, 44(7), 1702–1717.

[20] Donno, D., Beccaro, G. L., Mellano, M. G., Cerutti, A. K., & Bounous, G. (2015). Goji berry fruit (Lycium spp.): Antioxidant compound fingerprint and bioactivity evaluation. *Journal of Functional Foods*, 18, 1070–1085.

[21] Montesano, D., Cossignani, L., Giua, L., Urbani, E., Simonetti, M. S., & Blasi, F. (2016). A Simple HPLC-ELSD Method for Sugar Analysis in Goji Berry. *Journal of Chemistry*, 1-5.

[22] Wang, T., Yang, J., Li, H., & Wang, Y. (2019). Aminoclay decorated with lanthanide complexes and carbon dots: Tunable emission and information encryption. *Journal of Rare Earths*, 37(9), 995–1001.

[23] Li, J., Xia, D., Gao, M., Jiang, L., Zhao, S., & Li, G. (2021). Invisible luminescent inks and luminescent films based on lanthanides for anti-counterfeiting. *Inorganica Chimica Acta*, 526, 120541.

[24] Siddique, A.B., Singh, V. P., Chatterjee, S., Pramanik, A. K., & Ray, M. (2018). Facile synthesis and versatile applications of amorphous carbon dot. *Materials Today: Proceedings*, 5(3), 10077–10083.

[25] Kumar, P., Dwivedi, J., & Gupta, B. K. (2014), Highly luminescent dual mode rare-earth nanorod assisted multi-stage excitable security ink for anti-counterfeiting applications. *Journal of Materials Chemistry C*, 2(48), 10468–10475.

[26] Li, Q., Du, H., Li, J., Deng, J., Wang, R., & Chen, Y. (2022). Sulfur-rich carbon quantum dots based on Alternanthera philoxeroides and thiourea for the detection of tartrazine. *Journal of Materials Science: Materials in Electronics,* 33(16), 12808–12818.

[27] Krishnaiah, P., Atchudan, R., Perumal, S., Salama, E. S., Lee, Y. R., & Jeon, B. H. (2022). Utilization of waste biomass of Poa pratensis for green synthesis of n-doped carbon dots and its application in detection of Mn^{2+} and Fe^{3+}. *Chemosphere*, 286, 131764.

[28] Huang, Z. Y., Wu, W. Z., Li, Z. X., Wu, Y., Wu, C.-B., Gao, J., Guo, J., Chen, Y., Hu, Y., & Huang, C. (2022). Solvothermal production of tea residue derived carbon dots by the pretreatment of choline chloride/urea and its application for cadmium detection. *Industrial Crops and Products*, 184, 115085.

[29] Marouzi, S., Darroudi, M., Hekmat, A., Sadri, K., & Oskuee, R. K. (2021). One-pot hydrothermal synthesis of carbon quantum dots from Salvia hispanica L. seeds and investigation of their biodistribution, and cytotoxicity effects. *Journal of Environmental Chemical Engineering*, 9(4), 105461.

[30] Ge, L., Hu, G., Zhao, F., Wang, X., Ma, Z., & Liu, R. (2021). Carbon dots prepared by thermal reactions and selective detections of copper and mercury ions in visible spectrum. *Applied Physics A: Materials Science and Processing*, 127(5), 388.

[31] Wang, H. Y., Zhou, L., Yu, H. M., Tang, X. D., Xing, C., Nie, G., Akafzade, H., Wang, S. Y., & Chen, W. (2022). Exploration of Room-Temperature Phosphorescence and New Mechanism on Carbon Dots in a Polyacrylamide Platform and their Applications for Anti-Counterfeiting and Information Encryption. *Advanced Optical Materials,* 2200678, 1–11.

[32] Eskalen, H., Kavgacı, M., Kayış, A., & Özğan, Ş. (2021). One-Pot Synthesis of Carbon Quantum Dots and Their Application As a Fluorescent Inks. *Eskişehir Technical University Journal of Science and Technology A - Applied Sciences and Engineering*, 22(4), 366–377.

[33] Eskalen, H., Yaykaşlı, H., Kavgacı, M., & Kayış, A. (2022). Investigating the PVA/TiO_2/CDs polymer nanocomposites: effect of carbon dots for photocatalytic degradation of Rhodamine B. *Journal of Materials Science: Materials in Electronics,* 33(7), 4643–4658.

[34] Şen, F. B., Beğiç, N., Bener, M., & Apak, R. (2022). Fluorescence turn-off sensing of TNT by polyethylenimine capped carbon quantum dots. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 271, 120884.

[35] Kilic, B., Dogan, V., Kilic, V., & Kahyaoglu, L. N. (2022). Colorimetric food spoilage monitoring with carbon dot and UV light reinforced fish gelatin films using a smartphone application. *International Journal of Biological Macromolecules,* 209, 1562–1572.

[36] Uruş, S., Çaylar, M., Eskalen, H., & Özgan, Ş. (2022). Synthesis of GO@Fe_3O_4@TiO_2 type organic–inorganic nanohybrid material: Investigation of the effect of nanohybrid doped liquid crystal E7 and the photocatalytic degradation of ciprofloxacin. *Journal of Materials Science: Materials in Electronics,* 33(7), 4314–4329.

[37] Eskalen, H., Uruş, S., & Özgan, Ş. (2021). Microwave-Assisted Synthesis of Mushrooms Like MWCNT/SiO_2@ZnO Nanocomposite: Influence on Nematic Liquid Crystal E7 and Highly Effective Photocatalytic Activity in Degradation of Methyl Blue. *Journal of Inorganic and Organometallic Polymers and Materials,* 31(2), 763–775.

[38] Marino, C., Cabanero, J., Povia, M., & Villevieille, C. (2018). Biowaste Lignin-Based Carbonaceous Materials as Anodes for Na-Ion Batteries. *Journal of The Electrochemical Society,* 165(7), 1400–1408.

[39] Rai, S., Singh, B. K., Bhartiya, P., Singh, A., Kumar, H., Dutta, P. K., & Mehrotra, G. K. (2017). Lignin derived reduced fluorescence carbon dots with theranostic approaches: Nano-drug-carrier and bioimaging. *Journal of Luminescence*, 190, 492–503.

[40] Das, P., Bhattacharyya, S. K., Banerji, P., & Das, N. C. (2021). Acoustic cavitation assisted synthesis and characterization of photoluminescent carbon quantum dots for biological applications and their future prospective. *Nano-Structures and Nano-Objects*, 25, 100641.

[41] Swapna, M. S. & Sankararaman, S. (2017). Carbon Nanonecklaces with Carbon Nanotubes and Carbon Dots. *International Journal of Materials Science*, 12(4), 541–548.

[42] Sivanandhan, M., Parasuraman, A., Surya, C., Lakshminarayanan, K., Krishnakumar, B., Mani, D., & Ahn, Y. H. (2022). Facile approach for green synthesis of fluorescent carbon dots from Manihot esculenta and their potential applications as sensor and bio-imaging agents. *Inorganic Chemistry Communications*, 137, 109219.

[43] Xu, D., Lei, F., Chen, H., Yin, L., Shi, Y., & Xie, J. (2019). One-step hydrothermal synthesis and optical properties of self-quenching-resistant carbon dots towards fluorescent ink and as nanosensors for Fe^{3+} detection. *RSC Advances,* 9(15), 8290–8299.

[44] Taspika, M., Permatasari, F. A., Nuryadin, B. W., Mayangsari, T. R., Aimon, A. H., & Iskandar, F. (2019). Simultaneous ultraviolet and first near-infrared window absorption of luminescent carbon dots/PVA composite film. *RSC Advances,* 9(13), 7375–7381.

[45] Kayış, A., Kavgacı, M., Yaykaşlı, H., Kerli, S., & Eskalen, H. (2021). Investigation of Structural, Morphological, Mechanical, Thermal and Optical Properties of PVA-ZnO Nanocomposites. *Glass Physics and Chemistry,* 47(5), 451–461.

[46] Pandiyan, S., Arumugam, L., Srirengan, S. P., Pitchan, R., Sevugan, P., Kannan, K., Pitchan, G., Hegde, T. A., & Gandhirajan, V. (2020), Biocompatible Carbon Quantum Dots Derived from Sugarcane Industrial Wastes for Effective Nonlinear Optical Behavior and Antimicrobial Activity Applications. *ACS Omega,* 5(47), 30363–30372.

[47] Gezici, S. (2022). Molecular Mechanisms, Biological and Pharmacological Properties of Goji Berries as a Potential Natural Antioxidant Medicine. *Mersin Üniversitesi Tıp Fakültesi Lokman Hekim Tıp Tarihi ve Folklorik Tıp Dergisi,* 12(1), 67–76.

[48] Beker, S. A., Truskewycz, A., Cole, I., & Ball, A. S. (2020). Green synthesis of: Opuntia-derived carbon nanodots for the catalytic decolourization of cationic dyes. *New Journal of Chemistry,* 44(46), 20001–20012.