Journal of Apitherapy and Nature/Apiterapi ve Doğa Dergisi, 1(1), 33-37, 2018

Apiterapi ve Doğa Dergisi
Journal of Apitherapy and Nature
www.dergipark.gov.tr/jan

Synthesis and Applications of Carbon Dots from Food and Natural Products: A Mini-Review

Gıda ve Doğal Ürünlerden Karbon Noktaların Sentezi ve Uygulamaları: Derleme

Saliha DINC[1*], Meryem KARA[2]

[1] Organic Farming Management, Çumra School of Applied Sciences, Selçuk University, Konya, Turkey
[2] Food Technology, Çumra Vocational High School, Selçuk University, Konya, Turkey
salihadinc@gmail.com

Received/Geliş Tarihi: 12/03/2018, **Accepted**/ Kabul Tarihi: 19/03/2018
***Corresponding author** /Yazışılan yazar

Abstract

Carbon dots with less than 10 nm sizes have been emerged as a fascinating tool in many areas with their non-toxic, biocompatible, water-soluble and easy synthesis merits. Bioimaging, biosensing, photocatalysis, drug delivery etc. are some applications of luminescent carbon dots. Carbon dots may be synthesized from any carbon sources including foods, food wastes, plants, chemicals, graphene etc. via top-down or bottom up methods. However, carbon dots can naturally be extracted from some foods, natural products such as honey, caramels and sugar beet molasses. In this paper, we tried to focus on synthesis and applications of carbon dots derived from food or natural products.

Keywords: Carbon Dots, Natural Products, Food, Synthesis, Application.

Özet

10 nm'den küçük boyutlara sahip karbon noktalar toksik olmayan, biyouyumlu, suda çözünür ve kolay sentezlenebilme avantajlarıyla birçok alanda büyüleyici bir araç olarak ortaya çıkmışlardır. Biyogörüntüleme, biyoalgılama, fotokataliz, ilaç salımı vs. lüminesans karbon noktaların bazı uygulama alanlarındandır. Karbon noktalar; gıdalar, gıda atıkları, bitkiler, kimyasallar, grafen gibi herhangi bir karbon kaynağından yukarıdan aşağıya ya da aşağıdan yukarıy metotlarıyla sentezlenebilirler. Bununla birlikte, karbon noktalar bazı gıdalar, bal, karamel ve şeker pancarı ya da şeker kamışı melasından doğal olarak ekstrakte edilebilirler. Bu makalede, gıda ya da doğal ürünlerden elde edilen karbon noktaların sentezi ve uygulama alanlarına odaklanmaya çalışılmıştır.

Anahtar Kelimeler: Karbon Noktalar, Doğal Ürünler, Gıda; Sentez, Uygulama.

1. INTRODUCTION

Carbon dots are fluorescent carbon nanomaterials that have sizes below 10 nm (Zhang &Yu, 2016). Since discovery of carbon dots, incidentally in 2004 by Xu et al., many studies showed outstanding properties of carbon dots compared to metal quantum dots. Some of these unique merits of carbon dots are easy and green synthesis, low toxicity, excellent biocompatibility, good photostability, good water solubility and low cost (Zhao et al, 2015; Zhang &Yu, 2016; Mandani et al., 2017). By considering these advantages, increasing trends of applications in imaging, sensing, photocatalysis, drug delivery, solar cells, light emitting diodes etc. are not surprising (Wen et al., 2015; Wang et al., 2017b, Dinc et al., 2017). Carbon dots contain sp^2/sp^3 carbon and oxygen containing groups such as carboxylic, carbonyl, hydroxyl groups etc. (Zhu et al., 2015). In addition, carbon dots derived from raw materials, having nitrogen involve nitrogen-based groups (Dinc et.al, 2017). The structure of carbon dots gives distinct optical properties (Zheng et al., 2015). The emission character of carbon dots changes with their size because of quantum confinement effects (Baker &Baker, 2010). As the size of carbon dots decreases, the emission colour shifts to the blue region. In other words, small carbon dots emit blue light; contrary big carbon dots emit yellow, green or red light depending on their size (Durmusoglu, 2017). Heteroatom doping, or surface passivation give better optical properties to carbon dots (Xu et al., 2016).

Any carbon source can be used to synthesize carbon dots, including food, plant, candle soot, waste, coal, chemicals etc. (Hu et al., 2016; Himaja et al., 2014). However, carbon dots can naturally be extracted from some food, food waste (Dinc, 2016). Fundamentally, synthesis methods of carbon dots are classified into top-down and bottom- up methods. In top-down methods, large carbon structure such as carbon nanotube, graphite etc. are broken down to carbon dots. Arc-discharge, laser- ablation and electrochemical synthesis methods are defined as top-down methods (Baker &Baker, 2010). In contrast to top-down methods, bottom- up approaches are generally described that carbon dots are formed from molecular precursors. Hydrothermal method, microwave –assisted method, combustion or thermal routes, supported routes are the examples of bottom-up methods (Baker &Baker, 2010).

This mini review summarized the studies about carbon dots derived from natural or food sources. In this article, we tried to focus on the presence / synthesis methods of carbon dots from natural or food sources as well as their applications.

2. PRESENCE OF CARBON DOTS IN NATURAL / FOOD SOURCES

So far, carbon dots have naturally found / extracted in various foods that are bread, caramel, baked lamp, nescafe (Jiang et al., 2014; Sk et al., 2012; Wang et al, 2017a). Heating is mostly used to prepare these mentioned foods. Carbon dots can be formed during heating process (Sk et al., 2012). In the study by Wang et al.(2017a), blue-emitting carbon dots were extracted from lamb baked at 250°C for 30 minutes Li et al. (2018) investigated carbon dots derived from Maillard reaction. Maillard reaction is known as non- enzymatic browning reaction, formed between reducing sugar and free amino groups (Yıldız et al., 2010). Maillard reaction forms in bread, caramel, baked lamp during heating process (Yıldız et al., 2010). In the study by Li et al. (2018), glucose and lysine were used and heated at 180 °C for 10 hour. Synthesized carbon dots from Maillard reaction gave blue fluorescent under ultraviolet light. The work by Sk et al. (2012) showed food carbon dots formed at high temperature are smaller than those at low temperature. Interestingly, in the study by Mandani et al. (2017) carbon dots have found in raw honey to which heating is not applied. Mandani et al. (2017) reported generation of carbon dots during honey formation by bee.

Dinç (2016) showed presence of blue-emitting carbon dots extracted with water from sugar beet molasses by-product of sugar beet refining process. Presence of carbon dots in sugar beet molasses may be attributed to heat process applied during sugar production like in foods.

3. SYNTHESIS OF CARBON DOTS USING NATURAL / FOOD SOURCES

Carbon dots have been synthesized from variable food and natural sources generally using heating in domestic microwave oven and hydrothermal heating. Carbon dots are generated via pyrolysis or carbonization of molecular precursors under high temperature (Zuo et al., 2015). Optical properties of carbon dots change with heating temperature, time, carbon precursors and solvent.

Carbon dots were synthesized from various natural sources including orange juice, lemon juice, papaya powder, orange peel, pollen and sugar cane molasses etc. using hydrothermal routes (Sahu et al., 2012; Hoan et al., 2017; Wang et al., 2016; Prasannan &Imae, 2013; Wang et al., 2015; Huang et al., 2017). Teflon –lined stainless steel autoclave is used in hydrothermal method with the temperature above 150 °C and time period varying from 4 h to 12 h. Commonly, water or ethanol are used as solvent. The colour of solution containing source and solvent change from colourless to brown –dark brown colour with hydrothermal heating.

Carbon dots from yogurt, honey was synthesized via microwave heating (Dinc et al, 2017; Wu et al., 2013). Carbon dots have been synthesized via microwave heating at shorter times compared to hydrothermal heating. Domestic microwave oven is generally used at different wattage levels such as 500 W, 800W etc. and with less than one hour. Water / ethanol mixture and water are used as solvent. Brown solution is obtained with microwave heating similar to that of hydrothermal heating.

Apart from these, De and Karak (2013) reported the synthesis of carbon dots from banana juice via heating 150°C for 4 h and Baruah et al. (2014) showed the synthesis of carbon dots from Assam tea via heating at 200°C for 10 h totally.

Furthermore, centrifugation, dialysis, filtration, silica gel column is used to purify carbon dots (Baker &Baker, 2010; Gude et al., 2016).

4. APPLICATIONS OF CARBON DOTS DERIVED FROM NATURAL / FOOD SOURCES

Recently, utilization of carbon dots in many areas including bioimaging (Dinc et al., 2017; Yang et al., 2014; Kasibabu et al., 2015), sensing (Yu et al., 2015; Zhu et al., 2013), patterning and coding (Zhu et al., 2013) catalysis (Hutton et al., 2017) have drawn considerable attraction. Some applications of carbon dots in bioimaging, sensing and catalysis are presented as follow:

Biocompatible carbon dots synthesized from yogurt via microwave synthesis successfully used in imaging of colon epithelial cells. Toxicological assessment of yogurt carbon dots showed no toxic effects on healthy CoN cells and MCF-7 breast cancer cells up to 7.1 mg/mL carbon dot concentration (Dinc et al., 2017).

Fluorescent carbon dots synthesized from pomegranate fruits using hydrothermal method were used in bioimaging of *Pseudomonas aeruginosa* and *Fusarium avenaceum* (Kasibabu et al., 2015).

Haber et al. (2016) produced carbon dots from citric acid and glucosamine using domestic pressure cooker. Resulting carbon dots with bright, stable and wavelength-dependent fluorescence were utilized in imaging of mice embryonic fibroblast cells with almost no cytotoxic effect up to 0.667 mg/mL carbon dot concentrations (Laber et al., 2016).

Atchudan et al. (2017) reported a utilization of nitrogen-doped carbon dots from Chionanthus retusus fruit extract as a biological probe for investigation of *Candida albicans* and *Cryptococcus neoformans* strains in fluorescent microscope. Orange juice was used as a natural precursor in synthesis of carbon nanoparticles by Sahu et al. (2012). Strong fluorescent carbon dots showed no cytotoxicity on osteosarcoma MG-63 cells and were efficiently taken up by these cells.

Carbon dots originated from honey exhibited successful performance in sensitive and selective detection of Fe^{3+} (Yang et al., 2014). Yu et al. (2015) described the green, low-cost, water-soluble fluorescent carbon dots preparation of carbon dots from Jinhua bergamot via hydrothermal method. The prepared carbon dots were successfully used in detection of Hg^{2+} and Fe^{3+} (Yu et al., 2015).

Dinc (2016), extracted carbon dots from sugar beet molasses without using any additional process. Extracted carbon dots exhibited strong blue fluorescence under UV light. These carbon dots were used as a sensing probe for detection of riboflavin and tetracycline.

Wang et al. (2016) reported a simple-one step hydrothermal green approach to prepare carbon dots from papaya powder. As prepared carbon dots were used as a potential probe for fluorescence sensing of *E. coli* O157:H7.

Carbon dots synthesized from chitosan and functionalized with sodium fluoride can selectively detect retinoic acid (Majumdar et al., 2018).

Carbon dots prepared by pyrolysis of leaves (palm, bamboo, camphor, ginkgo etc.) were used as a fluorescent sensing platform for Fe^{3+} detection (Zhu et al., 2013).

Orange peel derived fluorescent carbon dots loaded with ZnO obtained using hydrothermal carbonization method were used as a photocatalyst for degradation of naphthol blue-black azo dye under UV irradiation (Prasannan &Imae, 2013).

5. SUMMARY AND OUTLOOK

Carbon dots are rising stars of carbon nanomaterials. In this mini-review, we summarized the synthesis and applications of carbon dots derived from natural and food sources. Notably, synthesis methods of carbon dots are simple, green and low-cost. Besides, application of carbon dots is various including medicine, sensor, solar cell computer etc. We think that synthesis methods and application areas of carbon dots are increasingly developing. Therefore, we aimed to draw attention to carbon dots, to encourage future studies in this paper.

REFERENCES

Atchudan, R., Edison, T. N. J. I., Chakradhar, D., Perumal, S., Shim, J.J., Lee, Y.R. (2017). Facile green synthesis of nitrogen-doped carbon dots using *Chionanthus retusus* fruit extract and investigation of their suitability for metal ion sensing and biological applications, *Sensors and Actuators B*, 246, 497–509

Baker, S.N., Baker, G.A. (2010). Luminescent carbon nanodots: Emergent nanolights. *Angew. Chem. Int.* 49, 6726–6744

Baruah, U., Gogoi, N., Konwar, A., Deka, M, J, Chowdhury, D. & Majumdar, G. (2014). Carbon Dot Based Sensing of Dopamine and Ascorbic Acid, *Journal of Nanoparticles* (http://dx.doi.org/10.1155/2014/178518)

De, B., Karak, N. (2013). A green and facile approach for the synthesis of water soluble fluorescent carbon dots from banana juice, *RSC Adv*., 3, 8286–8290

Dinc, S. (2016). A simple and green extraction of carbon dots from sugar beet molasses: Biosensor applications. *Sugar Industry*, 9, 141 (1–5).

Dinc, S., Kara, M., Demirel Kars, M., Aykül, F., Çiçekci, H., Akkuş, M. (2017). Biocompatible yogurt carbon dots: evaluation of utilization for medical applications. *Applied Physics A*, 123 (572) (DOI 10.1007/s00339-017-1184-y)

Durmuşoğlu, E. G. (2017). Kuantum Nokta, (https://www.metalurji.org.tr/dergi/dergi160/d160_3134.pdf).

Gude, V., Das, A., Chatterjee, T. & Mandal, P.K. (2016). Molecular origin of photoluminescence of carbon dots: aggregation-induced orange-red emission, *Phys. Chem. Chem. Phys*., 18, 28274-28280

Himaja, A.L., Karthik, P.S., Sreedhar, B., Singh, S.P. (2014). Synthesis of carbon dots from kitchen waste: Conversion of waste to value added product. *Journal of Fluorescence*, 24,1767–1773

Hoan, B.T., Huan, V.P., Van, N. H., Nguyen, D.Y., Tam, P.D., Nguyen, K.T., Pham, V-H. (2017) Luminescence of lemon- derived carbon quantum dot and its potential application in luminescent probe for detection of Mo6+ ions, Luminescence, 1-7

Hu, S., Wei, Z., Chang, Q., Trinchi, A., Yang, J. (2016). A facile and green method towards coal-based fluorescent carbondots with photocatalytic activity, *Applied Surface Science*, 378, 402-407

Huang, G., Chen, X., Wang, C., Zheng, H., Huang, Z., Chen, D. & Xiee, H. (2017). Photoluminescent carbon dots derived from sugarcane molasses: synthesis, properties, and applications, *RSC Adv*., 7, 47840–47847

Hutton, G. A.M., Martindale, B.J.M., Reisner, E. (2017). Carbon dots as photosensitisers for solar-driven catalysis, *Chemical Society Reviews*, 46, 6111-6123

Jiang, C., Wu, H., Song, X., Ma, X., Wang, J., Tan, M. (2014). Presence of photoluminescent carbon dots in Nescafe original instant coffee: Applications to bioimaging, *Talanta* 127, 68–74

Kasibabu, B. S.B., D'souza, S.L., Jha, S., Singhal, R.K., Basu, H., Kailas, S.K. (2015). One-step synthesis of fluorescent carbon dots for imaging bacterial and fungal cells, *Analytical Methods*, 7, 2373-2378

Laber, C.H., Essner, J.B., Scott, T.A., Polo-Parada, L., Baker, G.A. (2016). Domestic pressure cooker as inexpensive hydrothermal vessel: Demonstrated utility for eco-friendly synthesis of non-toxic carbon dots, *Nano-Structures & Nano-Objects*, 6, 52–58.

Li, D., Na, X., Wang, H., Xie, Y., Cong, S., Song, Y., Xu, X., Zhu, B-W.&Tan, M. (2018). Fluorescent Carbon Dots Derived from Maillard Reaction Products: Their Properties, Biodistribution, Cytotoxicity, and Antioxidant Activity, *Journal of Agricultural and Food Chemistry*, 66, 1569-1575

Majumdar, S., Bhattacharjee, T., Thakur, D., Chowdhury, D. (2018). Carbon Dot based Fluorescence sensor for Retinoic acid, *Chemistry Select*, 3, 673 –677.

Mandani, S., Dey, D., Sharma, B., Sarma, T.K. (2017). Natural occurrence of fluorescent carbon dots in honey. *Carbon*, 119, 569-572

Prasannan, A. Imae, T. (2013). One-Pot Synthesis of Fluorescent Carbon Dots from Orange Waste

Peels, *Industrial & Engineering Chemistry Research*, 52, 15673−15678.

Sahu, S., Behera, B., Maiti, T.K., Mohapatra, S. (2012). Simple one-step synthesis of highly luminescent carbon dots from orange juice: application as excellent bio-imaging agents, *Chemical Communication*, 48, 8835–8837

Sk, M.P., Jaiswal, A., Paul, A., Ghosh, S.S., Chattopadhyay, A. (2012). Presence of amorphous carbon nanoparticles in food caramels. *Scientific Reports*,383 (2), 1–5

Wang, H., Xie, Y., Liu, S., Cong, S., Song, Y., Xu, X. & Tan, M. (2017a). Presence of fluorescent carbon nanoparticles in baked lamb: Their properties and potential application for sensor, *Journal of Agricultural and Food Chemistry* (DOI: 10.1021/acs.jafc.7b02913)

Wang, N., Wang, Y., Guo, T., Yang, T., Chen, M., Wang, J. (2016). Green preparation of carbon dots with papaya as carbon source for effective fluorescent sensing of Iron (III) and *Escherichia coli*. *Biosensors and Bioelectronics*, 85, 68-75.

Wang, Z., Yuan, F., Li, X., Li, Y., Zhong, H., Fan, L. &Yang. S. (2017b). 53% Efficient Red Emissive Carbon Quantum Dots for High Color Rendering and Stable Warm White-Light-Emitting Diodes, *Advanced Materials*, (DOI: 10.1002/adma.201702910)

Wen, J., Xu, Y., Li, H., Lu, A. & Sun, S. (2015). Recent applications of carbon nanomaterials in fluorescence biosensing and bioimaging, *Chemical Communications*, 51, 11346-11358

Wu, L., Cai, X., Nelson, K. Xing, W., Xia, J., Zhang, R., Stacy, A.,J, Luderer, M., Lanza, M.,G., Wang, L.V., Shen, B. & Pan, D. (2013) A green synthesis of carbon nanoparticles from honey and their use in real-time photoacoustic imaging, *Nano Research*, 6(5): 312–325

Xu, Q., Kuang, T., Liu, Y., Cai, L., Peng, X., Sreepcad, T.S., Zhao, P., Yu, Z., Li, N. (2016). Heteroatom-doped carbon dots: Synthesis, characterization, properties, photoluminescence mechanism and biological applications, *Journal of Materials Chemistry B* (DOI: 10.1039/C6TB02131J.)

Xu, X., Ray R., Gu, Y. Ploehn, J.H., Gearheart, L., Raker, K. & Scrivens, W.A. (2014). Electrophoretic Analysis and Purification of Fluorescent Single-Walled Carbon Nanotube Fragments, *Journal of the American Chemical Society*, 126, 12736-12737

Yang, X., Zhuo, Y., Zhu, S., Luo, Y., Feng, Y., Dou, Y. (2014). Novel and green synthesis of high-fluorescent carbon dots originated from honey for sensing and imaging, *Biosensors and Bioelectronics*, 60, 292–298

Yıldız, O., Sahin, H., Kara, M., Aliyazıcıoğlu, R., Tarhan, Ö., Kolaylı, S. (2010). Maillard Reaksiyonları ve Reaksiyon Ürünlerinin Gıdalardaki Önemi, Akademik Gıda 8(6), 44-51

Yu, J., Song, N., Zhang, Y.K., Zhong, S.X., Wang, A.J., Chen, J. (2015). Green preparation of carbon dots by Jinhua bergamot for sensitiveand selective fluorescent detection of $Hg^{2+}$and Fe^{3+}, *Sensors and Actuators B*, 214, 29–35.

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

Zhang, J., Yuan, Y., Liang, G. & Yu, S-H. (2015) Scale-Up Synthesis of Fragrant Nitrogen-Doped Carbon Dots from Bee Pollens for Bioimaging and Catalysis, *Advanced Science*, 2, 1500002

Zhao, A., Zhaowei, C., Zhao, C., Gao, N., Rena, J., Qua, X. (2015). Recent advances in bioapplications of C-dots, *Carbon*, 85, 309 – 327

Zheng, X.T., Ananthanarayanan, A. Luo, K.Q. & Chen, P. (2015). Glowing Graphene Quantum Dots and Carbon Dots: Properties, Syntheses, and Biological Applications, *Materials Views*, 11(14), 1620-1636

Zhu, L., Yin, Y., Wang, C.F., Chen, S. (2013). Plant leaf-derived fluorescent carbon dots for sensing, patterning and coding, *Journal of Material Chemistry C*, 1, 4925.

Zhu, S., Song, Y. Zhao, X., Shao, J., Zhang, J. & Yang B. (2015). The photoluminescence mechanism in carbon dots (graphene quantum dots, carbon nanodots, and polymer dots): Current state and future perspective, *Nano Research*, 8(2), 355-381

Zuo, P., Lu, X., Sun, Z., Guo ,Y., He, H. (2015). A review on syntheses, properties, characterization and bioanalytical applications of fluorescent carbon dots, Microchim Acta (DOI 10.1007/s00604-015-1705-3).