Carbon quantum dot synthesis from indigo plant (*Indigofera tinctoria* .L)

Abstract

One of the main challenges of making Nano catalysts is the selection and preparation of suitable modifiers. The present study reports the synthesis of carbon Nano dots by a low-cost hydrothermal method using Indigofera tinctoria leaf extract as a novel carbon precursor. The optical properties of CQDs were analyzed by UV-visible spectroscopy and fluorescence studies. Surface morphology, functional groups and crystallinityof CQDs were evaluated by HR-TEM, FT-IRand XRD methods, respectively. The spherical appearance of the synthesized CQDs was confirmed by HR-TEM and the calculated size of the CQDs was 4 nm. XRD and SAED pattern results provide evidence for the amorphous nature of the prepared CQDs. Thermal stability of CQDs was studied by TGA analysis. The obtained CQDs acted as a green Nano catalyst.

Keywords: Green, synthesis, carbon quantum dots Indigo plant

Introduction

Carbon-based nanomaterial's such as carbon nanotubes,[1], graphene oxide,[2], fullerenes,[3], and Carbon quantum dot [3].have been playing vital roles in science and technology in the past two decades. Among these, Carbon quantum dot (CQDs) is fluorescent carbon nanomaterial's that have been engaged at the forefront of recent research [4]. Carbon quantum dot(CQDs) are nanoparticles 1–10 nm in size, which were unexpectedly discovered by Anbu et al. during the purification of single-walled carbon nanotubes in 2004[5]. The properties of the CQDs mainly depend on two factors: first, the choice of the carbon source (raw material), and second, the synthesis method. CQDs are quite divergent from other carbon-based nanomaterial's due to their exclusive outstanding properties, such as high water dispensability, strong chemical inertness, fluorescence, excellent photo stability, less toxic nature, excellent bio-compatibility, environmental friendliness, low cost and flexibility in surface modification[8-9].CQDs have multipurpose applications in various fields, such as drug delivery, optoelectronic devices, sensing of metal ions, biological imaging, biomolecules, catalysis, solar cells, and the oxygen reduction reaction[6].

CQDs have been synthesized by various top-down methods; including laser ablation, ultrasonic treatment, arc-discharge, and electrochemical and chemical oxidation, and bottom-up methods such as hydrothermal carbonization, microwave irradiation, pyrolysis, and plasma treatment [7]. Among these synthesis methods, arc discharge and laser ablation processes need highly expensive instruments, whereas electrochemical oxidation and chemical oxidation need strong acids. The microwave irradiation method demonstrates a simple way to synthesize CDs within few minutes; this method can be restricted by uncontrollable reaction conditions. The hydrothermal method is simplistic, quick, and economical, has a simple experimental setup, is and eco-friendly when compared to other synthesis methods. Carbon dots with tunable degrees of carbonization usually consist of carbon (C), oxygen (O), and hydrogen (H) decorated with various functional groups on their surfaces. Using inexpensive and eco-friendly biomass sources such as Phyllanthusemblica, prickly pear cactus, rice bran, Cocciniaindica, and sweet potatoes as carbon precursors to harvest CQDs has attracted great attention because of their green approach [8].The plant extracts containing citric acid, tartaric acid, and ascorbic acid act as efficient carbon precursors for the synthesis of highly fluorescent CQDs. The fluorescence properties of CQDs are influenced by solvents, size, pH, and dopants used during the synthesis. Recently, surface functionalization on CQDs was achieved by doping heteroatoms (such as boron, sulphur, nitrogen, and phosphorous). The functionalization of nitrogen tremendously increases the optical properties of CQDs when compared to undoped CQDs. At the same time, other important features of CQDs, such as the quantum yield (QY) and fluorescence lifetime are significantly improved by the functionalization approach. Further, the heteroatom doping affects the internal sharing of electrons in CDs and thus can change the band gap energy, which results in escalated fluorescence intensity of CQDs [9].These functionalized CQDs act as remarkable fluorescent probes in bio-imaging, catalysis, and chemo-sensing applications.[10].

Among carbon materials, CQDs are considered as a new generation material with excellent electron transfer capability, a suitable alternative to other carbon competitors. CQDs offer a high potential to replace traditional semiconductor quantum dots due to their unique luminescence performance, smaller size, good solubility, biocompatibility, increased adsorption capacity of reactive substrates, and low toxicity. Also, these compounds have many applications in the development of biological imaging, medical diagnosis, catalysis, etc. CQDs can be prepared from natural materials such as fresh mint leaves banana peel scraps, etc. [11].

The indigo plant belongs to the legume family and its original habitat was India. Indigo root and stem, bitter taste and laxative effect.Ithas expectorant and anti-parasite worms and strengthens hair. All parts of this plant reduce inflammation have and use them to treat chronic bronchitis, asthma (especially in children), hemorrhoids, insect bites and poisonous reptiles, It is used to treat wounds and skin disorders, in terms of the chemical compounds in the plant, including endical substances, endoxyl, There is isatan and labenzim, and the color extracted from this plant in ancient civilizations, such as Mesopotamia, Egypt, Greece, Rome, England, Central America, Peru, Iran and Africa have been known[12]. The study aimed to green synthesize of carbon quantum dots from a native plant called Indigo or Indigo with the scientific name Indigofera Tinctoria L. Indigo is a medicinal-industrial plant belonging to the legume family, which is cultivated in the south of Iran (Shoushtar)[13]. The components of Indigo plant are: alkaloids, glycosides, flavonoids, tannins, and phenolic compounds, amino acids, carbohydrates, mineral compounds, other compounds such as ash, ash soluble in acid, ash soluble in water, etc.Our goal in this research is to prepare quantum dot carbon using natural resources such as indigo plant with a hydrothermal method [14].

Fig 1. Chemical structure of indigo carmine (indigo blue dye)

Materials and methods

Chemicals and reagents

Indigofera tinctoria leaves were collected from Shoushtar city, Khuzestan province, Iran. Ammonia blue, methylene blue, methyl orange, sodium borohydride and polyvinyl alcohol (PVA) were purchased. All laboratory grade chemicals and reagents were used except for additional purification. Double distilled water was used for solution preparation and other purposes throughout the study.

Extract preparation

Freshly collected leaves of Indigofera tinctoria (50 g) were carefully washed with distilled water to remove impurities. The cleaned leaf was homogenously ground in an electric stirrer by adding 100 mL of double distilled water. The mixture was heated continuously at 30 °C, stirred for 1 h and then filtered, first using Whatman filter paper and then by centrifugation at 10,000 rpm for 15 min. Finally, the supernatant was collected and used as a carbon source for the synthesis of CQDs.

Synthesis of CQDs

In this study, carbon quantum dot was synthesized by a hydrothermal method from Indigo as precursors in deionized water at 200 °C for 14 h.The sample was dried in an oil bath and washed three times with ethanol. Finally, the resulting black powder was dried in a vacuum oven for 6 hours.

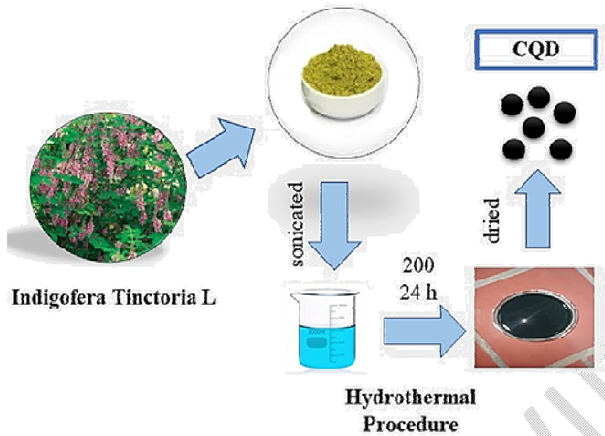

Fig 2.Quantum dot carbon extraction method from indigo plant

Results & Discussion

Figure3. Presents the FT-IR spectrum of the CQD. The broad peak at 3357 cm^{-1} confirms the stretching vibration of the O-H bond of the acidic and alcoholic functional group. The peak at 2931 cm^{-1} shows the stretching vibration of the C-H bond of SP^3. At 2364cm^{-1} C-H SP^2 stretching vibration of benzene ring of carbon dot structure and at 1591cm-1 N-H bending vibration is confirmed. The peak at 1416cm^{-1} O-H bending vibration is related to acidic and alcoholic functional groups. The two peaks at 1650cm^{-1} and 1078cm^{-1} show the stretching vibration of C=C and C-O, respectively. The peaks in the area of 672-751cm^{-1} show the bending vibration of C=C.

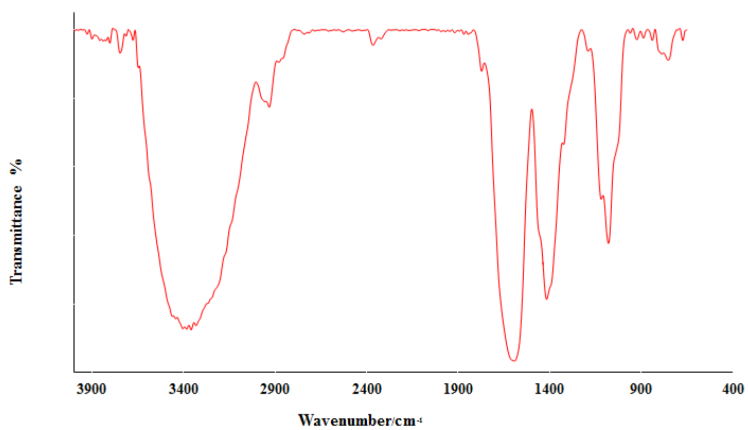

Fig 3. FT-IR of prepared sample

Figure 4 shows the uv-vis analysis of the sample in the range of 190-400nm in water solution. The peak in the region of 210 nm represents the electron transfer π to π* of C=C double bonds and the peak at 250 nm represents the n to π* electron transfer caused by the pair of non-bonding electrons of nitrogen or oxygen.

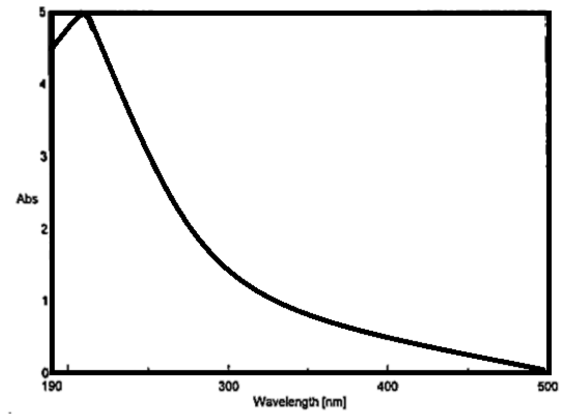

Figure 4.Uv-Vis of sample

Figure 5.Extract extracted from the indigo plant

Conclusion

Considering the importance of using carbon materials to modify the electrode surface and the features mentioned for carbon quantum dot, we prepared carbon quantum dot using indigo plant and with a hydrothermal method. Carbon quantum dot prepared by methods such as IR and UV.etc. We identified and checked. The synthesized material can be used to modify the electrode surface in sensing applications, corrosion, etc. This work can be a model for preparing carbon quantum dots from other natural sources.

References

1. Z. Zhao, J. Liu, M. Qin, K. Kou, G. Wu, H. Wu,.2020.EfectivecocatalystPt/PtOnanodots on La2O3 microspheres for degradation ofmethyl orange. J. Nanosci. Nanotechnol. 20, 3140–3147 .

2. M. Qin, D. Lan, J. Liu, H. Liang, L. Zhang, H. Xing, T. Xu, H.Wu,.2019. Synthesis of single-component metal oxides with controllablemulti-shelled structure and their morphology-related applications.Chem. Rec. 19, 1–19.https://doi.org/10.1002/tcr.201900017

3. L. Zhang, M. Qin, Y. Yu, M. Zhang, X. Zhao, J. Qian, H. Wu,.2019.Preparation of ternary Pt–NiO–ZnO hybrids and investigation ofits photocatalytic performance toward methyl orange. J. Mater.Sci. Mater. Electron. 30, 5158–5169 .

4. H. Wu, G. Wu, Y. Ren, X. Li, L. Wang,.2016.Multishelled metal oxidehollow spheres: easy synthesis and formation mechanism. Chem.A Eur. J. 22, 8864–8871.

5. Z. Zhao, J. Liu, H. Gong, G. Wub, H. Wu,.2019.Pt/Ni0.17Zn0.83O hybridswith enhanced photocatalytic performance: efect of reductiontreatments. Results Phys. 14, 102434

6. Wang, K. Maeda, A. Thomas, K. Takanabe, G. Xin, J.M. Carlsson, K. Domen, M. 2009.Antonietti, A metal-free polymeric photocatalyst for hydrogen production from water under visible light. Nat.Mater. 8(1), 76.

7. Z. Yi, J. Ye, N. Kikugawa, T. Kako, S. Ouyang, H. 2010. Stuart-Williams, H. Yang, J. Cao, W. Luo, Z. Li, An orthophosphate semiconductor with photooxidationproperties under visible-light irradiation. Nat. Mater. 9(7), 559 .

8. X. Wang, K. Maeda, X. Chen, K. Takanabe, K. Domen, Y. Hou,X. Fu, M.2019.Antonietti, Polymer semiconductors for artifcial photosynthesis: hydrogen evolution by mesoporous graphitic carbonnitride with visible light. J. Am. Chem. Soc. 131(5), 1680–1681

9. K. Kaviyarasu, E. Manikandan, J. Kennedy, M. Maaza,.2015. A comparative study on the morphological features of highly orderedMgO:AgOnanocube arrays prepared via a hydrothermal method.RSC Adv. 5, 82421–82428.

10. R.M. Shereema, T.P. Rao, V.S. Kumar, T.V. Sruthi, R. Vishnu, G.R. Prabhu and S.S. Shankar, Materials Science and Engineering: C, 2018 , 93, 21.

11. M. Algarra, A. González-Calabuig, K. Radotić, D. Mutavdzic, C.O. Ania, J.M. Lázaro-Martínez, J. Jimenez-Jimenez, E. Rodríguez-Castellón and M. Del Valle, Talanta, 2018, 178, 679.

12. M.R. Zargaran Khouzani, Central Asian Journal of Environmental Science and Technology Innovation, 2022, 3, 32.

13. M.R. Zargaran Khouzani, A.R. Siahpoosh and M.A. DaeiNaseri, The first national conference on the application of modern chemical and agricultural researches in the development of medicinal plants, 2021, 37.

14. M. Moalem-Banhangi, N. Ghaeni and S. Ghasemi, Synthetic Metals, 2021, 271, 116626.