ScienceDirect

Journal of Electroanalytical Chemistry
Volume 943, 15 August 2023, 117609

Electrochemical sensor based on N,P–doped carbon quantum dots derived from the banana flower bract (Musa acuminata) biomass extract for selective and picomolar detection of dopamine

A. Padmapriya [a], P. Thiyagarajan [b], M. Devendiran [c], R.A. Kalaivani [a], A.M. Shanmugharaj [d]

Show more

Share Cite

https://doi.org/10.1016/j.jelechem.2023.117609
Get rights and content

Highlights

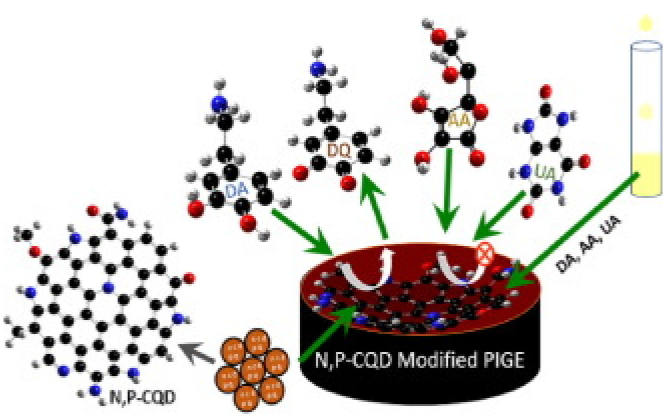
- Green synthesis method of heteroatoms doped carbon quantum dots (CQD) from Musa accumulata extract was proposed.
- Average particle size of the CQDs determined using TEM is ~3.5 nm.
- Paraffin wax impregnated graphite electrode (PIGE) was modified with CQDs.
- Picomolar level detection of dopamine was demonstrated using CQD modified graphite electrode.

- Fabricated CQD/PIGE electrode without Nafion coating renders selective detection of dopamine.

Abstract

A facile route was proposed in preparing phosphorus and nitrogen dual carbon quantum dots (N,P-CQD) from banana flower bract extract by hydrothermal synthesis for selective and reliable detection of catecholamines such as dopamine (DA). By morphologically characterizing the synthesized CQD using Transmission Electron Microscopy (TEM), it is discovered that its average particle size is 3.8 nm. While the doping of the heteroatoms upsurges the electrical conductivity of the CQD, the presence of the functional sites like acid (–COOH), (–NH_2) and phosphate (-PO_4^{3-}) groups selectively attract the cations *via.,* an ion-exchange mechanism leaving behind the anions, due to the electrostatic repulsion. The synthesized N,P-CQD/PIGE electrode-based electrochemical sensors demonstrated high selectivity and sensitivity for DA with a relatively low limit of detection (LOD) (~500 pM) and a wide linear range, extending from 6.0 μM to 0.1 mM. The N,P-CQD's detection selectivity is further validated by utilizing a combination with a somewhat larger concentration of uric (UA) and ascorbic (AA) acids and only a modest amount of DA. Additionally, the N,P-CQD/PIGE electrode successfully detects DA with a LOD as low as 630 pM and a larger linear range of 2.5 M to 0.16 mM in real-time samples of dopamine injection.

Graphical abstract



Download: Download high-res image (186KB)

Download: Download full-size image

Paraffin impregnated graphite (PIGE) based electrochemical sensor fabricated using banana bract extract derived N, P-doped carbon quantum dots (N, P-CQDs) selectively detect the dopamine neurotransmitter at the picomolar level concentrations.

Introduction

The human brain's neural networks process enormous amounts of information from the environment via senses including hearing, touch, and sight, which are then integrated with signals throughout the body [1]. Neurotransmitters (NTs), which are endogenous chemical messengers, are utilized by neurons to communicate with one another, affect muscle cells, or trigger a response in glandular cells. Human neurotransmitters mostly fall into the categories of amino acids (such as tyrosine and glutamic acid), biogenic amines (such as serotonin epinephrine, dopamine, and norepinephrine), and soluble gases (for ex., hydrogen sulfide, and nitric oxide) [2]. A catecholamine neurotransmitter, DA, is necessary to develop the mammalian central nervous system and hormones. When DA level is below normal can cause several neurological conditions, such as Huntington's disease, Parkinson's disease, and schizophrenia [3]. Many researchers are very interested in developing techniques and measuring catecholamine NTs since they may be utilized as therapeutically relevant biomarkers for particular illness states or to monitor the efficacy of therapies. DA concentrations can be measured in a range of biological fluids, including urine, platelets, saliva, serum, plasma, and cerebral spine fluids because NTs are found throughout the body [4]. As a result, quantitative assessment of NTs in various human systems is critical for screening, illness monitoring, and therapeutic approaches. (see Scheme 1.)

With their low cost, ease of miniaturization, ease of use, greater sensitivity, selectivity, speed, stability, dependability, and accuracy, electrochemical techniques stood out as having a quick response time [5]. Recent breakthroughs in nanotechnology aided in the blooming of innovative electrochemical sensors for DA determination that include the incorporation of nanoparticles [6], or graphene (GR) derivatives on an electrode surface [7], mesoporous carbons [8], carbon nanotubes (CNT) [9], and complex nanocomposites [10], using various nanomaterials and/or additional electrocatalysts utilized in the production of modified electrodes. The use of chemically modified electrodes (CME) is growing as a result of their advantages in terms of less challenging manufacturing techniques, increased electrochemical catalytic activity, and physical toughness [11]. Notably, DA coexists in extracellular fluids with other interfering substances such as tryptophan (Trp), ascorbic acid (AA), and uric acid (UA). The electrochemical method attracted attention because of its quick detection, simplicity, repeatability, excellent cost-effectiveness, and miniaturization potential [10].

In South India, bananas are grown on more than one lakh hectares, and this harvesting produces more than 10 million tons of bio-waste annually. The objective is to manage this enormous amount of bio-waste. Culinary banana bract is a dietary fiber (DF) by-product of banana farming that is rich in antioxidants. Owing to its numerous health advantages, especially in preventing and treating chronic and degenerative diseases, this antioxidant DF is extremely substantial [12]. As a result, it makes sense to use food waste as a starting material in the CQD preparation. The composition of chemicals, anti-bacterial, and anti-oxidant capacity properties of the bracts of bananas (Musa acuminata) were studied. The outcome of the imminent analysis showed a significant amount of raw protein, raw fiber, fat content, and carbohydrate in Musa acuminata. The cellulose and lignin content of the bract sample M. acuminata is estimated as (34.61±1.06%; 9.13±0.31%). Hence, M. Acuminata is chosen as a biomass precursor [13].

CQD is a new emerging carbonaceous nanomaterial that has piqued the research community owing to its beneficial properties. Usually, CQD is an advantageous substitute for semiconductor quantum dots in biological and chemical analysis because they typically have few valuable properties, such as fluorescence, biocompatibility, phenomenal up conversion, exceptional photostability, less toxicity, and are typically less than 10nm in size [14], CQD is frequently formed on macroscopic carbon structures using either chemical or physical cutting processes such as graphite, carbon nanotubes, carbon powders, and carbon fibers [15]. Hydrothermal and microwave treatment of organic precursors is another option for CQD synthesis [16], [17]. When compared to other synthetic techniques, the hydrothermal process is straightforward, affordable, and capable of producing a range of CQD in a single step. CQD disperses efficiently in water due to the presence of hydroxy, carboxyl, and epoxy groups on its surface. These functional groups not only give excellent dispersibility in water but also provide photoluminescent (PL) CQD. Finally, surface modification using heteroatom doping can boost the quantum yield of CQD [18]. In addition, by controlling the size of CQD via the quantum detention effect, one may control the electromagnetic, optical, and electrochemical properties [19]. CQD research has recently generated a lot of enthusiasm due to its apparent promise in analytical applications [20], [21], [22].

In the present study, the one-step hydrothermal aided technique was adopted for the synthesis of pristine and heteroatom (N,P-CQD, *N*-CQD, and P-CQD) doped carbon quantum dots from banana bract extract. To understand the structural, morphological, and chemical structures of the prepared CQDs, various characterization techniques such as UV–Visible spectroscopy, X-ray diffractometer (XRD), Fourier Transform Infrared (FT-IR), Raman spectroscopy, High-resolution Transmission Electron Microscopy (HR-TEM) and X-ray

Photoelectron Spectroscopy (XPS) were used. Subsequently, electrochemical sensors based on paraffin-impregnated graphite electrode (PIGE) was fabricated to detect dopamine, which was further characterized using various electrochemical tools such as Cyclic Voltammetry (CV), Chronoamperometry (CA), and Differential Pulse Voltammetry (DPV). Hetero atom doped carbon quantum dot (N,P-CQD) modified PIGE electrode detects ultralow concentrations (in picomolar) of dopamine, which is the first of its kind, and to date, no report has been made using paraffin-impregnated graphite (PIGE) electrodes.

Section snippets

Materials and method

Sigma Aldrich supplied the graphite rods. SRL chemicals, India supplied phosphoric acid and ethylene diamine. The analytes such as uric acid (UA), ascorbic acid (AA), and dopamine (DA) were procured from Himedia laboratories, India. Background electrolytes were prepared using double-distilled water before each experiment, and purified nitrogen gas was purged to eradicate dissolved oxygen.…

Synthesis of pristine, single, and dual-doped carbon quantum dots

The carbon source, banana flower bract was collected from a banana tree that had been planted in the house…

Results and discussion

Generally, CQD derived from bio-mass carbon sources have meager fluorescence qualities because of the lower heteroatom (such as N) concentration in the molecular backbone. Also, heteroatom doping techniques are an efficient method to effectively manipulate the optical and electronic properties of the CQD. Furthermore, doping of heteroatoms as well as surface functionalization of the CQD have a greater impact on the enhancement of their electrochemical properties. In terms of electron transfer,…

Conclusion

In Summary, novel nitrogen/phosphorus dual-doped carbon quantum dots (N,P-CQD) have been synthesized from banana bract biomass for electrochemical sensing of the dopamine neurotransmitter. Successful formation of ultralow low size (~3.5 nm) N,P-CQDs with turbostratic nature is corroborated using TEM and XRD. Raman spectroscopic characterization of the prepared CQDs revealed the presence of graphitic carbon with defective sites due to the doping of heteroatoms on the CQD surface. While the…

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.…

Acknowledgments

The authors were very grateful to the Central Instrumentation laboratory Vels University (VISTAS) and SRM University (XPS and TEM) characterization. I would like to thank Dr. P. Prabhu, Dr. S. Nehru, and Dr. B. Muthuraaman, University of Madras for their guidance, encouragement, and support in conducting my research work.…

Recommended articles

References (49)

J.M. Moon *et al.*
Conducting polymer-based electrochemical biosensors for neurotransmitters: a review
Biosens. Bioelectron. (2018)

A. Baranwal *et al.*
Clinical implications and electrochemical biosensing of monoamine neurotransmitters in body fluids, in vitro, in vivo, and ex vivo models
Biosens. Bioelectron. (2018)

D.T. Marc *et al.*

Neurotransmitters excreted in the urine as biomarkers of nervous system activity: Validity and clinical applicability
Neurosci. Biobehav. Rev. (2011)

N. Chauhan *et al.*
An electrochemical sensor for detection of neurotransmitter-acetylcholine using metal nanoparticles, 2D material and conducting polymer modified electrode
Biosens. Bioelectron. (2017)

X. Liu *et al.*
Highly sensitive determination of epinephrine by a MnO2/Nafion modified glassy carbon electrode
J. Electroanal. Chem. (2012)

H. Cheng *et al.*
Investigation of the electrochemical behavior of dopamine at electrodes modified with ferrocene-filled double-walled carbon nanotubes
Electrochim. Acta (2012)

M. Sajid *et al.*
Chemically modified electrodes for electrochemical detection of dopamine in the presence of uric acid and ascorbic acid: a review
TrAC - Trends Anal. Chem. (2016)

K. Ghosal *et al.*
Carbon dots: The next generation platform for biomedical applications
Mater. Sci. Eng. C (2019)

L. Li *et al.*
Quantitative detection of nitrite with N-doped graphene quantum dots decorated N-doped carbon nanofibers composite-based electrochemical sensor
Sens Actuators B Chem. (2017)

S. Li *et al.*
The development of carbon dots: From the perspective of materials chemistry
Mater. Today (2021)

View more references

Cited by (11)

Materials and design strategies for the electrochemical detection of antineoplastic drugs: Progress and perspectives

2024, Materials Science and Engineering R: Reports

Show abstract

Carbon quantum dots with ultra-high quantum yield for versatile turn-on sensor of gluten and cyanide Ions

2024, Dyes and Pigments

Show abstract

Defective graphene-nanomaterials derived from banana-biomass for simultaneous electrochemical detection of xanthine, hypoxanthine, and uric acid: Insights from scanning electrochemical microscopy on edge and basal planes

2024, Electrochimica Acta

Show abstract

Synthesis of carbon quantum dots from waste Phaseolus vulgaris for the development of a fluorescence sensing probe to detect plasticizer in cookies

2024, Process Safety and Environmental Protection

Show abstract

Carbon dots – A deep dive into their electrochemical applications

2024, Comprehensive Analytical Chemistry

Show abstract

Bio-functionalized carbon dots for signaling immuno-reaction of carcinoembryonic antigen in an electrochemical biosensor for cancer biomarker detection ↗

2024, Discover Nano

View all citing articles on Scopus ↗

View full text