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Electrochemical Determination of Phytohormone Using Nitrogen Doped Carbon Dots Modified Glassy Carbon Electrode

R. Pandiyarajan¹, R.Anitha², R.Karthikeyan^{2*}

PG student, Department of Chemistry, Parvathy's Arts and Science College, Dindigul, Tamil Nadu, India¹

Assistant Professor, Department of Chemistry, Parvathy's Arts and Science College, Dindigul, Tamil Nadu, India²

ABSTRACT: This paper depicts the highly sensitive electrochemical determination of salicylic acid using nitrogendoped carbon dots (N-CDs) modified glassy carbon (GC) electrode. N-CDs were prepared from L-asparagine and prepared N-CDs attached to the GC electrode by simply immersing in the alkaline solution of N-CDs without any linker. The attachment of N-CDs on GC electrode was confirmed by X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), scanning electron microscopy (SEM), electrical impedance spectroscopy (EIS) and cyclic voltammetry. X-ray photoelectron spectrum of N-CDs shows a peak at 285.3 eV due to C-N bond confirmed the attachment of N-CDs on GC substrate through C-N linkage. The N-CDs modified electrode shows an excellent electrocatalytic activity towards the oxidation of SA was achieved for the first time by amperometry method. Further, the current response was increased linearly with increasing SA concentration in the range 50 ×10-9 M to 20 ×10-6 M and the detection limit found to be $1.74 \times 10-9$ M (S/N=3). The practical application of the present modified electrode was effectively shown by measuring the concentration of SA in commercially available aspirin tablets and tomato leaf extract.

KEYWORDS: Nitrogen-doped carbon dots: salicylic acid: amperometry: aspirin

I. INTRODUCTION

Salicylic acid (SA) is a versatile phytohormone with important roles in various physiological processes in plants such as flowering, seed germination, growth, nodulation, respiration and photosynthesis. SA is widely used as an analgesic and anti-inflammatory agent. It was initially separated from the leaves and barks of willow [1]. It is employed topically for keratolytic, bacteriastatic, antifungal and photoprotective properties [2]. SA inhibits the activity of cyclooxygenase (COX) an enzyme responsible for the production of pro-inflammatory mediators like the prostaglandins, activates the AMP kinase, a key regulator of cellular ATP levels [3]. SA and its derivatives are wellknown to assist prevent cancer, reduce the chance of heart attack and improve diabetic conditions [4]. Tobacco plants treated with aspirin exhibited enhanced immunity to tobacco mosaic virus (TMV) [5]. A fascinating and remarkable general principle is that low concentrations of SA enhance the antioxidant capacity of plants, but high concentrations of SA cause cell death or susceptibility to abiotic stresses [6]. The optimal levels for the highest stress tolerance range from 0.1 mM to 0.5 mM for most plants [7]. The therapeutic range of salicylate is 15-30 mg/dL [8]. They indirectly directly or have an effect on the foremost organ systems within the body by uncoupling oxidative phosphorylation, inhibiting citric acid cycle enzymes and the amino acid synthesis [9]. Salicylism, the syndrome of SA toxicity is acute or chronic and develops a concentration of SA in blood serum concentrations higher than 35 mg/ml [10]. It leads to cause tinnitus [11], hypoprothrombinemia [12], hyperventilation [13], Reye syndrome [14], respiratory alkalosis [15], tachycardia [16] and metabolic acidosis [17]. So, it is very important to determine the concentration of SA in human blood serum in the clinical point of view. Among the wide variety of analytical techniques for the determination of SA [18-22], electrochemical methods received much attention due to its low cost, more selective and sensitive, high reproducible and less time consuming. Regardless, electrode fouling brought on by an electropolymerized uninvolved SA-film on the terminal is a major challenge for the electrochemical determination of SA. SA is determined by electrochemical method by different nanomaterials modified electrodes including metal nanoparticles [23-25], graphene [26], carbon nanotubes [27] and polymer composite modified electrodes [28], these electrodes involve a



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tedious fabrication procedure, high cost and difficult synthetic methods and lack of sensitivity towards practical application.

Carbon dots recently discovered nanosized carbon allotropes (NCAs) that have attracted the greatest interest due to their wondering fluorescent properties, mainly their excitation wavelength dependent emission [29]. The fluorescence of CDs may be due to the functional groups present on the surface, the size of the graphite core as well as type of carbon backbone [30]. CDs attracted intensive attention in recent years due to their applications in bioimaging [31], catalysis [32], biosensors [33], dye-sensitized solar cells [34] and light emitting devices [35].

In this study, we made an attempt to develop an electrochemical sensor for SA based on nitrogen doped carbon dots (N-CDs) modified glassy carbon electrode. First, the nitrogen doped carbon dots were prepared from L-asparagine by pyrolysis method. The prepared N-CDs were characterised by UV-visible, FT-IR spectroscopy, HR-TEM analysis. Further, the N-CDs were attached to the glassy carbon electrode surface by simply immersing into the alkaline solution of N-CDs by Michael's like nucleophilic substitution reaction. The N-CDs modified electrode characterised by cyclic voltammetry, electrical impedance spectroscopy and scanning electron microscopy techniques. The electrocatalytic activity of N-CDs modified electrode was examined by studying the oxidation of SA. The practical application of GC/N-CDs electrode was demonstrated by measuring the concentration of SA commercially available aspirin tablets.

II. EXPERIMENTAL SECTION

Chemicals and reagents: L-asparagine was purchased from Sigma. Salicylic acid was purchased from Merck. 0.2 M phosphate buffer (PB) solution (pH 7.2) was prepared using $Na_2HPO_4.2 H_2O$, $NaH_2PO_4.2H_2O$. Double distilled water was used to prepare all the solutions used in that investigation. Glassy carbon (GC) plates were purchased from Alfa Aeaser. Indium Tin oxide (ITO) plates were purchased from Ashi Beer optical Ltd, Japan. All other chemicals used in this investigation were of the analytical grade used without further purification. 0.2 M phosphate buffer solution (PB solution, pH 7.2) was prepared using Na2HPO4.2H2O and NaH2PO4.2H2O and the pH of the solution was adjusted with orthophosphoric acid and NaOH. Aspirin tablets were purchased from the local medical shop. 2.2. Instrumentation

UV-visible absorption spectra were obtained using JASCO V-550 UV-visible spectrophotometer. Fluorescence spectral measurements were performed on a JASCO FP-8500 spectrofluorometer equipped with xenon discharge lamp. The FT-IR measurements were recorded using Thermo fisher-Nicolet-iS5 spectrophotometer. HR-TEM images were taken from JEOL JEM 2100, USA operating at 200 kV. XRD analysis was carried out with X-ray diffraction unit Rigaku, USA using Ni-filtered Cu K \perp (λ =1.5406) radiation. XPS measurement was carried out using Shimadzu axis 165 high-performance multi-technique analysis. SEM measurements were carried at VEGA3 TESCAN, Czech Republic. The electrochemical measurements were performed in a conventional two-compartment, three electrode cell with mirror polished 3 mm GC electrode as a working electrode, PT wire as a counter electrode and NaCl saturated Ag/AgCl electrode as a reference electrode. For differential pulse voltammetry measurements, a pulse width of 0.06 s, the amplitude of 0.05 V, a sample period of 0.02 s and a pulse period of 0.20 s were used. All the electrochemical measurements were at room temperature.

Preparation of N-doped CDs: N-doped CDs were prepared by pyrolysis of L-asparagine. Briefly, 0.5 g of L-asparagine was heated to 100° C in a heating mantle. It was liquated after 10 min and the colourless solution was changed to brown within 20 min. The obtained brown colour solution was diluted by adding 50 mL of 10 mg/mL NaOH.

Modification of N-CDs on GC electrode: The GC electrode was polished with 0.05 µm alumina slurry and rinsed thoroughly with water. The polished GC electrode was sonicated in water for 15 min to remove the adsorbed alumina particles. The cleaned electrode was then immersed into the colloidal solution of 1 mL of N-CDs for 8 h. The N-CDs were attached to GC electrode through Michael's nucleophilic addition of an amine group on the olefinic bond present on GC electrode. This electrode is termed as GC/N-CDs electrode. For SEM and XPS measurements, GC plates were used as a substrate and for XRD measurements, ITO plates were used as a substrate with the similar modification procedure.



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III. RESULTS AND DISCUSSION

Characterization of N-CDs by UV-visible, FT-IR, HR-TEM and spectrofluorimetry: The electronic spectroscopy is one of the simplest techniques to characterise the CDs. The UV-visible absorption spectra recorded for asparagine and N-CDs are shown in Fig. 1. The N-CDs show an absorption band at 207 nm along with a shoulder band around 307 nm (curve a), corresponding to π - π * and n- π * transitions, respectively. On the other hand, an aqueous solution of asparagine does not show any absorption band around 307 nm (curve b).



Fig 1 UV visible spectra obtained for (a) l-Asparagine and (b) N-CDs

The FT-IR spectroscopy was used to identify the functional groups present on the surface of the N-CDs. FT-IR spectrum obtained for asparagine is shown in Fig.2. It shows bands characteristics of C=O, $-NH_2$ and -OH functional groups at 1648, 3380 and 3440 cm⁻¹, respectively. The FT-IR spectrum obtained for liquid N-CDs shows a band at 1634 cm⁻¹ due to the C=O stretching vibration of the amide group and a broad band obtained at 3345 cm⁻¹ corresponds to both $-NH_2$ and -OH groups (Fig. 2). These results suggest that the surface of N-CDs contains hydroxyl and carboxylic groups and $-NH_2$ group. Due to the presence of these hydrophilic groups, the N-CDs had an excellent water solubility.





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Fig 2 FT-IR spectra obtained for (a) liquid N-CDs and (b) N-CDs modified GC substrate

The size and the morphology of N-CDs are examined by HR-TEM analysis. Fig.3 shows the HR-TEM image of N-CDs. It shows that the N-CDs were roughly spherical in shape with the average size of 2.48±0.02 nm.



Fig 3 HR-TEM images obtained for CDs. Inset: SAED pattern of CDs. (B) Average size distribution plot for CDs

Characterization of N-CDs modified electrode by XPS, XRD, ATR-FT-IR and SEM analysis: For XPS and SEM analysis, the GC plate was sonicated with acetone and ethanol for 10 min and rinsed with double distilled water. The cleaned GC plate was immersed into the colloidal solution of 1 mL of N-CDs for 8 h. The GC plate was dried in a nitrogen atmosphere. For XRD and measurement, ITO plates were used as a substrate with similar modifications. XPS was used to confirm the attachment of N-CDs on the substrate. Fig. 4A shows the XPS survey spectrum of N-CDs modified GC substrate.



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Fig 4 (A) XPS survey spectrum, (B) C1s spectra, (C) N1s spectra and (D) O1s spectra obtained for N-CDs modified substrate

It shows peaks around 285, 400 and 532 eV corresponding to C 1s, N 1s and O 1s region of N-CDs modified substrate. Fig. 4B shows C 1s region of N-CDs modified substrate. It shows peaks at 284.3, 285.3, 286.4 and 288.4 eV corresponds to C=C/C-C, C-N, C-O and C=O/C=N bonds, respectively. The N 1s region shows the peaks at 398.6, 399.5 and 400.3 eV corresponds to C-N-C, (C)3-N and N-H bonds, respectively (Fig. 4C). Fig. 4D shows O 1s region for various oxygen functional groups. It shows peaks at 531.7 and 533.3 eV corresponding to C-O-C/C-OH and C=O bonds, respectively. The appearance of C-N bond confirms the attachment of N-CDs on GC substrate through C-N linkage. The N-CDs modified substrate was further characterised by XRD. The XRD pattern of N-CDs modified ITO plate is shown in the Fig.5. The diffraction peaks appeared at 26.30°, 33.39°, 37.70° and 39.56° corresponding to graphitic carbon planes of C (002), C (111), C (020) and C (021), respectively, confirming the successful attachment of N-CDs on the electrode surface.



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Fig 5 XRD pattern obtained for (a) GC/N-CDs substrate.

The size and morphology of N-CDs modified substrate were characterised by SEM analysis. Fig. 6 shows the SEM image obtained for N-CDs modified GC substrate. The N-CDs were uniformly distributed on the GC surface and the size of the N-CDs was found to be 28 nm after attached on the GC surface.



Fig 6 SEM image of N-CDs modified GC substrate

Characterization by cyclic voltammetry: The attachment of N-CDs on GC electrode surface was characterised by cyclic voltammetry technique. Fig.7 shows the cyclic voltammograms (CVs) obtained for bare GC and GC/N-CDs electrodes in the presence of 1 mM [Ru(NH3]6]Cl3 in 0.2 M PB solution (pH=3) at a scan rate of 50 mV s-1. The bare GC electrode shows a reversible peak with a peak separation of 67 mV corresponding to the [Ru(NH3)6]3+/2+ redox couple. However, after attachment of N-CDs, it shows the reversible redox peak with enhancement in the current. The self-assembled monolayer of N-CDs on GCE gives an efficient pathway for electron transfer. The electrochemical surface area of the electrode (A) can be calculated from Randles-Sevcik equation (1).

$$_{\rm D} = 2.69 \times 10^5 \,{\rm n}^{3/2} \,{\rm AD}^{1/2} \,{\rm Cv}^{1/2}$$
 (1)

Where, ip is maximum current (A); n is number of electrons transferred in redox event (n=1 for Ru (NH3)6Cl3 redox probe), A is the electrode area (cm2), D is the diffusion coefficient (9.1×10-6 cm2 s-1 for Ru(NH3)6Cl3), C is the concentration of the redox probe (1 mol/cm3); \perp is the scan rate (50 mV s-1). The electrode active area of N-CDs



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modified electrode was calculated to be 0.1071 cm2 which is almost 1.5 times larger than the geometric area of bare GC electrode (0.07 cm2).

Where, i_p is maximum current (A); n is number of electrons transferred in redox event (n=1 for Ru (NH₃)₆Cl₃ redox probe), A is the electrode area (cm²), D is the diffusion coefficient (9.1×10⁻⁶ cm² s⁻¹ for Ru(NH₃)₆Cl₃), C is the concentration of the redox probe (1 mol/cm³); v is the scan rate (50 mV s⁻¹). The electrode active area of N-CDs modified electrode was calculated to be 0.1071 cm² which is almost 1.5 times larger than the geometric area of bare GC electrode (0.07 cm²).



Fig 7 CVs obtained for 1 mMRu(NH3)6Cl3 at (a)bare GC and (b) GC/N-CDs electrodes in 0.2 M PB solution (pH 3) at a scan rate of 50 mV s-1.

Characterization by Electrical impedance spectroscopy: Electrical impedance spectroscopy (EIS) is used to investigate the conductive nature of the bare GCE and GCE/N-CDs. Fig.8 shows the Nyquist, Bode-phase angle and Bode-amplitude plots for bare GC and GC/N-CDs electrodes in 1 mM Ru(NH3)6Cl3 in 0.2 M phosphate buffer solution (pH 3) at scanning frequencies from 0.01 to 100000 Hz. Fig.8A shows the Nyquist plots obtained for bare GC and GC/N-CDs electrodes. The charge transfer resistance (Rct) can be calculated from the semi-circle obtained in the Nyquist plot. Bare GCE shows the Rct value of 40.96 k Ω whereas the N-CDs modified electrode exhibit the 18.12 $k\Omega$. The decrease in Rct value reveals that the electron transfer reaction is more facile in the GCE/N-CDs. Fig. 8B shows the Bode-phase angle plot for bare GC and GC/N-CDs electrodes. It is well known that if the phase angle greater than or equal to 90°, the electrode behaves like an ideal capacitor, indicating the insulating nature of the electrode [36]. On the other hand, if the phase angle is less than 90° then, the electrode is allowing ions into the surface area of the electrode. Electron transfer reaction was facile through the pinholes or defects in the modified electrode. It can be seen from the figure that the values of the phase angle of both bare GCE and GCE/N-CDs less than 90° and thus the electrodes did not behave like an ideal capacitor. Therefore, the term capacitor C is replaced by constant potential element (CPE) in the equivalent circuit. The GCE/N-CDs have less phase angle (73°) when compared to bare GCE (85°). The decrease in the phase angle value for GCE/N-CDs suggests that N-CDs act like a conducting channel which facilitates the electron transfer reaction between the redox probe and underlying GCE. Fig. 8C shows the Bode-amplitude plots for bare GCE and GCE/N-CDs. It can be seen from the figure, at higher



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frequencies, the values of |Z| are almost constant for both bare GCE and GCE/N-CDs. At lower frequencies, the total impedance is equal to the sum of Rs and Rct values. The charge transfer resistance (Rct) value drastically decreased after the attachment of N-CDs on bare GCE. The heterogeneous electron transfer rate constant (ket) can be calculated from bare GC and GC/N-CDs electrodes using the following equation (2).

$$\mathbf{k}_{\rm et} = \mathbf{R}\mathbf{T}/\mathbf{n}^2\mathbf{F}^2\mathbf{A}\mathbf{R}_{\rm ct}\mathbf{C}$$
(2)

Where, R is the gas constant, T is the temperature (298 K), F is the Faraday constant (96,485 C), A is the area (0.07 cm²), R_{ct} is the charge transfer resistance, C is the concentration of redox couple in the bulk solution and n is the number of electrons transferred per molecule.(n=1 for Ru(NH₃)₆^{3+/4+} redox couple) The calculated k_{et} values are 0.92× 10^{-3} cm s⁻¹ and 2.1×10⁻³ cm s⁻¹ for bare GCE and GCE/N-CDs respectively.



Fig 8 (A) Nyquist, (B) Bode – phase angle plots and (C) Bode amplitude ^{Frequency (Hz)} plots for (a) bare GC and (b) GC/CDs modified electrodes in 1mM K₃[Fe(CN)₆] containing 0.2 M PB solution (pH 7.2) at scanning frequencies from 0.01 to 100 000 Hz.

The higher k_{et} value obtained for GC/N-CDs electrode indicates that the electron transfer reaction was faster at GC/N-CDs electrode compared to bare GC electrode.

Electrochemical behaviour of SA at GC/N-CDs electrode: Figure.9 shows that the cyclic voltammograms (CVs) obtained for 0.5 mM SA at bare GC and GC/N-CDs electrodes in 0.2 M PB solution (pH 7.2) at a scan rate of 50 mV s-1. The bare GC electrode shows an oxidation peak at 0.98 V corresponding to oxidation of SA on the forward scan. In the reverse scan, two small peaks at 0.43 V and 0.12 V corresponding to the reduction of electrochemical SA oxidation products. In the subsequent cycles, the oxidation peak of SA decreased due to the oxidation products of SA. (2,3- and 2,5- dihydroxybenzoic acids) and polymerization took place. These oxidation products caused electrode surface fouling. Due to the strong electrode fouling caused by electropolymerized passive SA film, the bare GC electrode is not suitable for the stable determination of SA. On the other hand, GC/N-CDs electrode shows a higher oxidation current for SA and 20 mV is less positive compared to the bare GC electrode. The GC/N-CDs electrode also showed 2-fold higher oxidation current compared to that of bare GC electrode. The higher oxidation current obtained for oxidation of SA due to the high surface area provided by N-CDs and strong π - π interaction between SA and N-CDs.



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Fig 9 CVs obtained at (a) bare GC and (b) GC/N-CDs electrodes for 0.5 mM SA in 0.2 M PB solution at a scan rate of 50 mV s-1.

Sensitive determination of SA at GC/N-CDs electrode: Since GC/N-CDs electrode gave stable response for SA, further; it can be utilised for the sensitive determination of SA. Figure.10 shows that the differential pulse voltammograms (DPVs) for each 20 \square M addition of SA at GC/N-CDs electrode in 0.2 M PB solution (pH 7.2). The addition of 20 \square M SA shows an oxidation peak at 0.90 V. Further, each increment of 20 \square M SA increases the oxidation current with a slight shift in the potential with a correlation coefficient of 0.9954. The obtained results suggest that the sensitive determination of SA is possible at N-CDs modified electrode.



Fig 10 DPVs obtained for each 20 µM of SA at GC/N-CDs electrode in 0.2 M phosphate buffer solution (pH 7.2).Inset: Calibration plot of concentration of SA vs. Oxidation current of SA.



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Figure.11 shows that DPVs obtained for SA oxidation in the wide range of concentrations from 0.001 to 1 mM at GC/N-CDs electrode in 0.2 M PB solution (pH 7.2). The oxidation peak current of SA is linearly increased while increasing the concentration of SA. There is a good linearity obtained between SA oxidation current and concentration of SA with a correlation coefficient of 0.9904. These results suggest that GC/N-CDs electrode is used for the sensitive determination of SA.



Fig 11 DPVs obtained at GC/N-CDs electrode for wide range concentration from 1 µM to 1 mM in 0.2 M PB solution (pH 7.2) Inset: calibration plot for the concentration of SA

Amperometric determination of SA using GC/N-CDs electrode: Amperometric method is used to examine the sensitivity of GC/N-CDs electrode towards the detection of SA. Fig.12 shows the amperometric i-t curve obtained for SA at GC/N-CDs electrode in homogeneously stirred 0.2 M PB solution at applied potential of +1.0 V. The modified electrode has shown an initial addition of 50 nM into the same solution with a sample interval of 50 s, the current response is linearly increased for further additions. The Amperometric current linearly is also increased, when the concentration of SA is increased from 50 nM to 20 mM at GC/N-CDs electrode with a correlation coefficient of 0.9991. The detection limit was found to be 1.74 nM (S/N=3).



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Fig 12 Amperometric i-t curve obtained for the determination of SA at GC/N-CDs electrode in 0.2 M PB solution. Each 50 nM additions (a-g), (h) 100 nM, (i) 200 nM, (j) 500 nM, (k) 1 μ M, (l) 2 μ M, (m) 5 μ M, (n) 10 μ M, (o) 20 μ M and (p) 50 μ M at a regular interval of 50 s. $E_{applied}$ = +1.0 V. Insset: Calibration plot amperometric current vs. concentration of SA.

Real sample analysis: The practical application of present modified electrode is demonstrated by measuring the acetylsalicylic acid present in the commercially available aspirin tablets. For real sample analysis, first one aspirin tablet is weighed, finely ground and dissolved in methanol and sonicated for 30 min and allow to settle, filtered to remove additives and fillers. Further, the filtrate was diluted 10 times with 0.2 M PB solution (pH 7.2). Fig.13 shows that the DPVs obtained for acetylsalicylic acid at GC/N-CDs electrode in 0.2 M PB solution. The GC/N-CDs electrode shows no oxidation in 0.2 M PB solution (curve a). The addition of aspirin to 0.2 M PB solution (pH 7.2) shows an oxidation peak at 0.92 V may be due to oxidation of salicylic acid (curve b). To confirm the observed peak at 0.92 V is due to oxidation of SA. We have added known concentration of commercial SA to the same solution.



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Fig 13 DPVs obtained at GC/N-CDs electrode for (a) Asprin tablet solution, (b) $50 \perp M$, (c) $100 \perp M$ and (d) $150 \perp M$ SA in 0.2 M PB solution (pH 7.2).

The addition of 50 μ M SA to the above solution, the oxidation current at 0.92 V is enhanced (curve c) indicating that the peak at 0.92 V was corresponding to the oxidation of SA. For further each addition of 50 μ M SA to the same solution, the oxidation current is increased linearly without a shift in the potential (curve d-e) The obtained results suggest that N-CDs modified electrode has been successfully used to measure the concentration of SA in commercially available aspirin tablets.

IV. CONCLUSIONS

The present work has demonstrated a simple, facile and reproducible method with N-CDs modified GC electrode, for electrochemical determination of SA. N-CDs have been prepared by pyrolysis method and immobilised on GC electrode through Michael's nucleophilic addition. The modified electrode is characterised by XRD, electrical impedance spectroscopy, SEM and XPS. The XPS study confirms that the N-CDs are attached to the GC substrate through C-N linkage. Further, it shows good electrocatalytic activity towards the oxidation of SA. The GC/N-CDs electrode shows higher oxidation current than that of the bare GC electrode due to the higher surface area provided by N-CDs and π - π interaction between SA and N-CDs. Using Amperometry, detection limit of 1.74 nM with a linear range of 50 nM to 20 \Box M has been achieved. Further, the practical application of present modified electrode was demonstrated by the determination of SA in commercially available aspirin tablets.

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