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Preparation and Characterization of Bhant Leaves-derived Nitrogen-doped Carbon and its Use as an Electrocatalyst for Detecting Ketoconazole

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Abstract: In this study, the electrocatalytic characteristics of nitrogen-doped carbon (NDC) prepared from *Clerodendrum Infortunatum* L leaves on a glassy carbon electrode (GCE) surface was evaluated with regards to its ability to detect the electroactive drug ketoconazole (KCZ). The NDC was prepared by carrying out a simple pyrolysis of dry powder of the leaves at 850 °C. The prepared NDC was characterized using field-emission scanning electron microscopy, energy dispersive spectroscopy, transmission electron microscopy, X-ray photoelectron spectroscopy and Brunauer-Emmett-Teller analysis, and was then used as an electrode material. The performance of the electrochemical KCZ sensor with the NDC-modified glassy carbon electrode (NDC/GCE) was found to be optimal when using PBS buffer at pH 3 and a concentration of 0.1 mg/ml of NDC in the conjugate with Nafion polymer. Under these conditions, the NDC/GCE displayed a KCZ detection limit of 3 µM and a linear dependence of its response on KCZ concentration over a wide range of KCZ concentrations from 47 µM to 752 µM ($R^2 = 0.9742$). These results confirmed the potential of NDC as an electrocatalyst.

Keywords: Ketoconazole · Electrochemical sensor · Glassy carbon electrode · Nitrogen-doped carbon · Bhant leaves.

1 Introduction

Gold, platinum and palladium are very commonly used as working electrodes in electroanalysis due to their good properties, e.g., high conductivity, mechanical and chemical stability, and good electrocatalytic properties [1]. However, their costs limit their practical application. Besides, carbon-based electrodes such as glassy carbon/ graphite pencil electrodes are quite popular due to their low costs as well as their high mechanical and chemical stability levels [1–3]. However, to effectively use these carbon-based electrodes, specifically to achieve high sensitivity and selectivity, they often need to be modified with a suitable electrocatalyst [4]. Carbon-based materials such as carbon nanotubes, graphene, fullerene, and carbon nanofibers have been extensively investigated as electrocatalysts in the past three decades [5]. However, their high costs constitute one of the barriers to commercialization. So from commercialization point of view, researchers have been trying to develop carbon based-electrocatalysts from inexpensive resources such as wild plants, agro-waste, etc [6–12]. Insertion of doping agents such as nitrogen and sulfur into carbon-based electrocatalysts has become quite popular for improving their electrocatalytic properties. Particularly, nitrogen doping has significant advantages as the nitrogen atom is more electronegative than the carbon atom owing to its two lone pairs on its valence shell. As a result, nitrogen-doped carbon (NDC) gives more chance to carbon to attract more positive species [13], which simplifies the electron transport reaction. In addition, doping carbon

with nitrogen enhances its surface wettability, which facilitates access of electrolyte ions/analytes to the pores in carbon materials. Moreover, the doping of carbon with nitrogen increases the electronic conductivity as the nitrogen dopant causes a shift in the Fermi level to the valence band in a carbon electrode. Therefore, nitrogen-doped carbon [14–16] has found good electrochemical applications. As the primary focus of our ongoing research is to find carbon materials that could act as potential electro-

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catalysts in the electrochemical sensor and biosensor arena, we have developed a simple method to prepare a nitrogen-doped carbon material and evaluated its feasibility as an electrocatalyst in the detection of the drug ketoconazole (KCZ).

As a source of carbon, we considered the typical medicinal plant *Clerodendrum Infortunatum* L. (locally known as Bhant), which is available in sufficient quantities in various countries of Asia including India, Bangladesh, Malaysia, Pakistan, Burma, Sri Lanka and Thailand. It is a wild plant and grows without any caretaking, producing a significant amount of leaves. The whole plant is used to treat swellings, stomachache, cholera, fever, diarrhoea, inflammation and joint pains [17–20]; its root and root back is used for coughs, asthma, anemia, colds, nervous disorders, as antidotes and as a bitter tonic [18,21]; and its leaf is used for inflammatory diseases, swelling, lung diseases, stomach pains, fever, eye complaints, digestive disorders and rheumatism [22,23]. However, there has been no report on preparing any carbon materials from this wild plant for any application including electrochemical sensor fabrication.

KCZ, commonly used as medicinal drug [24], has also found versatile use as an antifungal product, antidandruff shampoo, cream, tablet, etc. But the presence of excess KCZ in biological systems leads to urticaria, angioedema, leukopenia, haemolytic anemia, nausea and thrombocytopenia [25,26]. Most importantly, KCZ can inhibit the enzyme cytochrome-P450 [27], and some phase-II enzymes [28–31]. It is thus important to have in hand a sensitive, accurate and reliable way of detecting KCZ in various media including biological fluids, buffers, pharmaceutical formulations, and cosmetics.

As a cost-effective, reliable and quantitative detection methodology, electrochemical analysis has already proven its excellence. Thus, since the completion of investigations of the electrochemical properties of KCZ [32–37], various electrodes such as mercury electrodes [32], silver solid amalgam electrodes [33], boron-doped diamond electrodes [36], boron-doped diamond electrodes using square wave adsorptive voltammetry [38], GCEs [37], and CPEs [39,40] have been used to develop KCZ sensors. To obtain better electrochemical sensing performances, the bulk electrodes have been modified with various electrocatalysts such as MWCNTs [41], AuNPs [42,43], and β-cyclodextrin [44]. These electrocatalysts, however, are expensive. Thus finding cost-effective electrocatalysts remains a crucial endeavor.

In the current work, we prepared a homemade NDC from an inexpensive resource, namely Bhant leaves, for the fabrication of an electrochemical sensor of KCZ. The prepared NDC was characterized in detail using field-emission scanning electron microscopy (FESEM), energy dispersive spectroscopy (EDS), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy and Brunauer-Emmett-Teller (BET) surface area analysis, and then was tested as a sensing material. A GCE was modified with the NDC using the drop casting method.

To lower the detection limit for KCZ, the performance of the NDC/GCE was optimized in terms of experimental electrochemical parameters and the amount of NDC loaded.

2 Material and Methods

2.1 Chemicals

Bhant plant leaves were gathered from the west side of Mominpur, Keshabpur, Jessore, Bangladesh. High-purity nitrogen (N_2) gas was provided by the SCG, Jubail, KSA. Ketoconazole, ethanol, sodium chloride, potassium chloride, nafion, sodium hydroxide pellets, and hydrochloric acid were purchased from Sigma-Aldrich. Disodium monophosphate, potassium ferrocyanide ($K_4[Fe(CN)_6]$) and potassium ferricyanide ($K_3[Fe(CN)_6]$) were ordered from Duksan Pure Chemicals, Korea. Monosodium diphosphate was obtained from Scharlab S. L., Spain and a Ketoral tablet was supplied from a local pharmacy of Dhaka, Bangladesh.

2.2 Instrumentation

Sample morphology was visualized using a TESCAN LYRA 3 (Czech Republic) scanning electron microscope (SEM), while elemental composition was determined by acquiring energy dispersive X-ray spectra (EDS) using an Xmass detector (Oxford instruments) equipped within the SEM. High-resolution transmission electron microscopy (HRTEM) images were obtained using a JEM-2011 JEOL microscope. Surface chemical analysis of NDC was accomplished using an X-ray photoelectron spectrometer (XPS) equipped with an Al–Kα micro-focusing X-ray monochromator (ESCALAB 250Xi XPS Microprobe, Thermo Scientific, USA). BET-BJH analysis (Micromeritics ChemiSorb 2750) was performed to determine the specific surface areas and pore size distributions of the prepared porous carbon nanosheets. Voltammetric and impedimetric results were obtained using a single potentiostat CHI 660E instrument (USA). The three-electrode system utilized for the entire electrochemical analysis included an Ag/AgCl (3 M KCl) reference electrode, Pt wire counter electrode, and either a bare GCE (3 mm diameter) or NDC-modified GCE working electrode.

2.3 Preparation of NDC from Bhant

The Bhant plant leaves were cleaned using deionized (DI) water and were converted into small pieces, which were then dried in an electric oven at 100 °C for 12 h. The dried leaves were pulverized for 10 min using a household blender to make a fine powder. This fine powder was carbonized (heated) at 850 °C in a tube furnace under N_2 atmosphere for about 5 h. The carbon obtained after carbonization was washed two times with 0.5 M HCl and three times with distilled water, followed by an overnight drying at 60 °C to collect the dried NDC. Scheme 1 shows

Scheme 1. Schematic representation of the preparation of NDC from Bhant leaves.

a schematic representation of the NDC preparation process.

2.4 Preparation of NDC and Nafion Polymer Matrix Conjugate

The preparation process included first washing the glass vials and drying them in an oven. Then 0.5 ml of 0.5 % (v/v) Nafion® solution was added into the glass vials containing 9.5 ml of distilled water and the resulting mixture was stirred for 10 min. Nafion matrix was used for better dispersion of NDC in aqueous medium as well as efficient functionalization to the GCE surface through its functional groups. Generally, use of nafion also increase stability of the prepared carbon film. Various amounts (0.05 mg, 0.1 mg, and 0.2 mg) of NDC were then each added slowly to a separate Nafion® solution samples and each resulting mixture was sonicated for 60 minutes using an ultrasonicator. The vials containing conjugated NDC in the Nafion matrix were corked tightly and stored in a refrigerator.

2.5 Preparation of the Working Electrode

Before having its surface modified, a GCE (3 mm width) was polished using 0.3 mm alumina powder suspensions on a smooth cloth, and the polished electrode was ultrasonicated in and then rinsed with double-distilled water and finally allowed to air dry. Next, a volume of 20 µL of the NDC-conjugated Nafion matrix was drop-dried using a micro-pipette on the cleaned GCE. The film was dried in a normal aerial atmosphere for 20 min until the solvent had completely evaporated. Prior to carrying out the experiments to detect KCZ, the modified electrode was rinsed with double-distilled water. Scheme 2 shows the NDC conjugation with Nafion and preparation of the electrode used for sensing KC.

3 Results and Discussion

3.1 Characterization of NDC

The morphology of the as-prepared NDC was evaluated by acquiring FESEM images of the NDC at various magnifications as shown in Figure 1. Inspection of the lowest-magnification FESEM image (Figure 1(A)) showed NDC particle dimensions of < 20 µm. Inspection of the higher-magnification images (Figure 1 (B and C)) confirmed that each such microparticle was composed of interconnected nanosheets/nanoparticles and also clearly showed the presence of numerous pores in the prepared NDC.

Further surface characterization was carried out by acquiring TEM images. The TEM image at a typical magnification (Figure 2A) illustrated the architecture of the interconnected nanosheets, showing the presence of a very large number of channels and macropores, consistent with the FESEM images. An HRTEM image (Figure 2B) demonstrated the presence of many well-distributed mesopores. A selected area electron diffraction (SAED) analysis (Figure 2C) indicated that the prepared NDC was amorphous.

To determine the chemical composition of the NDC, XPS was employed. Figure S1(A) in the supporting information shows the XPS survey spectrum acquired from an NDC sample. Five different main peaks were observed, specifically located at 533.70, 401.22, 284.60, 154.60 and 103.60 eV, corresponding, respectively, to O1s,
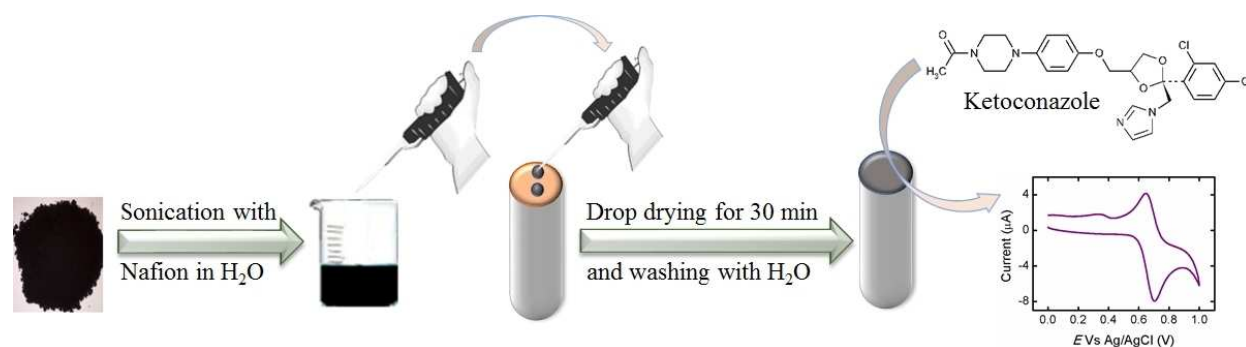
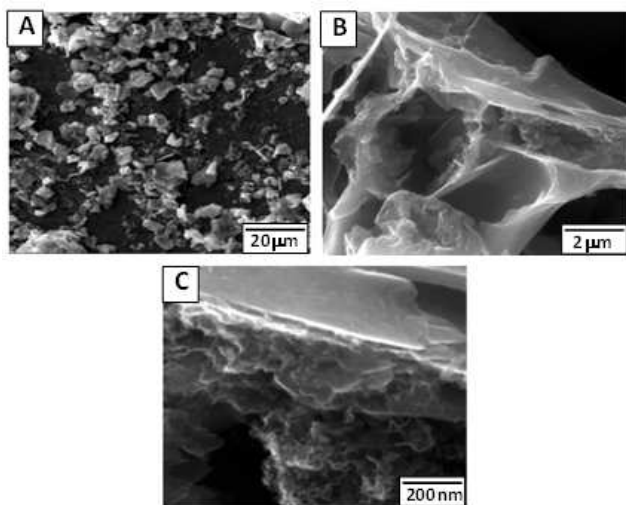Scheme 2. Schematic representation of the NDC-modified GCE used for sensing KCZ.

Fig. 1. FESEM images at various magnifications (A–C) of NDC prepared from Bhant leaves.
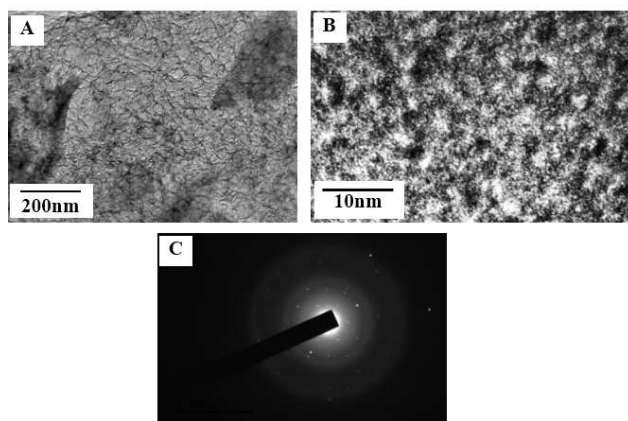

Fig. 2. (A) TEM, (B) HRTEM image, (C) and selected area diffraction of NDC prepared from Bhant leaves.

N1s, C1s, Si2s and Si2p. Figures S1(B), S1(C), and S1(D) in the supporting information show the high-resolution spectra of the C1s, N1s and O1s regions, respectively. This analysis confirmed the presence of nitrogen in the prepared carbon from Bhant; i.e. the prepared carbon was indeed doped with nitrogen. In addition to nitrogen, the presence of oxygen was also indicated, attributed to the commonly found introduction of oxygen into carbon materials prepared using pyrolysis. However, we were not able to separate the oxygen peaks of the carbon material from the oxygen peak of the glass, due to the overlap between these peaks.

Figure S2(A) in supporting information shows the N_2 adsorption-desorption isotherm acquired from the prepared NDC at 850 °C. It was observed to be a type-II/IV adsorption-desorption isotherm, indicative of a porous NDC [45]. Specifically the type H4 loop indicated that the NDC particles were mostly microporous and mesoporous [45,46], with the relatively high volumes at high relative

pressures (P/P0 = 0.80–1.00)) demonstrating the presence of macropores. The specific surface area of the porous NDC nanosheets and its pore volume were determined from the BET analysis to be 417.29 m^2/g and 0.2544 cm^3/g, respectively. The BET surface area was found to be higher than that of commonly employed carbon nanotubes [47,–48]. Figure S2(B) in supporting information shows the corresponding Barrett-Joyner-Halenda (BJH) pore-size distribution of the porous NDC nanosheets. A wide distribution of pore widths (1.94–202.6 nm) was observed, with an average pore width of 2.44 nm, which indicated the presence of micro-, meso-, and macropores in the NDC. Along with the relatively high specific surface area [49], the coexistence of micro-, meso-, and macropores provided much room for ions. As particles with well-distributed porous structures and large specific surface areas in general show improved electrochemical properties, the porous NDC nanosheets in the current work with their well-stratified porous structure and large specific surface areas were considered to have elite electrode properties for various electrochemical sensor applications.

3.2 Electrochemical Characterization of the NDC/GCE with Electrochemical Impedance Spectroscopy (EIS)

To determine the effect of the NDC on the GCE, EIS spectra were recorded (Figure 3). Here, the EIS technique was applied to measure the resistance of the electron transport of redox species $K_3[Fe(CN)_6]$ and $[K_4Fe(CN)_6]$ in a 1.0 M KCl solution on Bare as well as NDC modified GCE. In Figure 3A, the solution resistance (Rs) was 122 Ω on the bare GCE and was 103 Ω on the NDC/GCE; and the charge transfer resistance (Rct) was found to be 2132 Ω on the bare GCE and 780 Ω on the NDC/GCE. The data can be described well by the circuit in Figure 3B This low Rct value confirmed that NDC reduced the resistance to charge transfer between the iron complex and electrode surface.

3.3 Electrocatalytic Activity of the NDC/GCE in a KCZ Solution

A cyclic voltammetric (CV) analysis (Figure 4) of 500 μM KCZ in 0.1 M PBS (pH 3.0) on the bare GCE (green curve) showed an oxidation peak at 0.704 V and reduction peak at 0.644 V, clearly confirming its quasireversible behavior. The obtained CV response of the KCZ solution on the NDC/GCE (purple curve) indicated an enhanced electrochemical signal and revealed the feasibility of using NDC as an electrocatalyst. The oxidation and reduction signal in the CV responses were calculated to be, respectively, approximately 4.27 μA and 2.40 μA for the bare GCE, and increased to 7.95 μA and 4.13 μA for the NDC/GCE. But note that the modification of the electrode with NDC reduced the starting oxidation potential of KCZ. These analyses indicated the beneficial electrocatalytic properties of NDC for the electrochemical
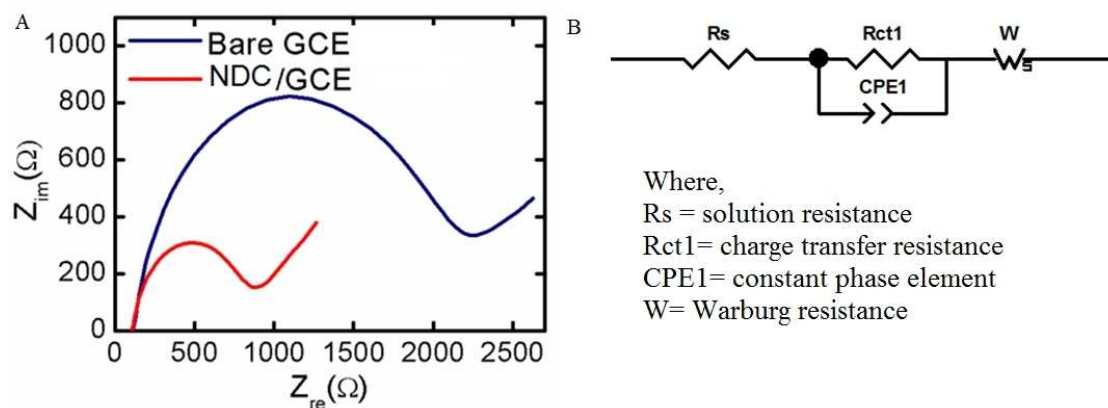
Fig. 3. (A) EIS plots using 2.5 mM $K_3[Fe(CN)_6]$ and 2.5 mM $[K_4Fe(CN)_6]$ in a 1.0 M KCl solution at the bare GCE and the NDC/GCE. A 0.1 mg/mL NDC solution was used to make the NDC/GCE and (B) Corresponding simulated circuit for impedence experiment.
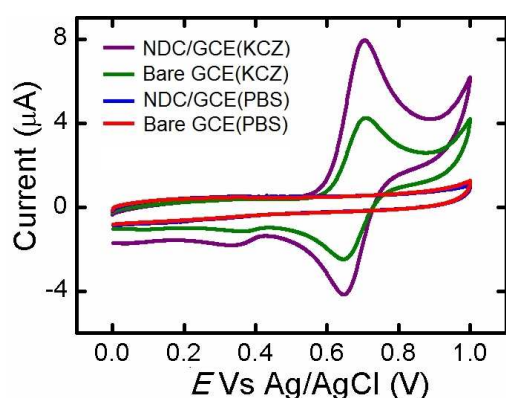

Fig. 4. Cyclic voltammograms of PBS buffer (pH 3.0) and 500 μM KCZ in PBS buffer (pH 3.0), each at scan rate of 100 mV/S, on the bare GCE and NDC/GCE surfaces. A 0.1 mg/mL NDC solution was used to make the NDC/GCE.

reaction of KCZ, which apparently resulting from NDC's high surface area and low resistance in the electron transfer reaction. Interestingly, a considerable signal amplification was observed for the oxidation signal (1.86 fold) than for the reduction signal (1.72 fold). Therefore, throughout our study of the detection of KCZ, we mainly focused on investigating the oxidation response rather than the reduction response. To understand the background response of supporting electrolytes on the NDC-modified surface, CV experiments of a blank PBS solution at both the bare GCE (red curve) and modified GCE (blue curve) were also conducted. Almost identical CV responses, i.e. background signals, were found; this result confirmed that the NDC did not increase the background response. Note that, in general, a background current must be low in order to achieve a low detection limit during electroanalysis.

3.4 Investigation of the Effect of pH, Loading of NDC and Scan Rate on the Electrochemical Sensing

To ensure an optimal performance of the KCZ sensor, the pH of the experimental solution was also investigated (Figure 5). Here, irreversible behavior and a poor electrochemical signal were observed for KCZ at high pH. The poor electrochemical properties of NDC at high pH might have been due to poor solubility of KCZ at such pH levels. Though higher pH (9.42) of NH_3–NH_4Cl buffer showed higher solubility and higher electrochemical signal [36], but interestingly in our experimental conditions, both the solubility and reversibility were improved at lower pH (≤ 4). Due to the good solubility, quasireversibility, and enhanced electrochemical signal at pH 3, this pH was used for the rest of the studies.

To determine the effect of the amount of NDC loaded on the GCE, we recorded CVs of KCZ using various NDC/GCEs prepared from different amounts of NDC. As shown in Figure S3 in supporting information, the
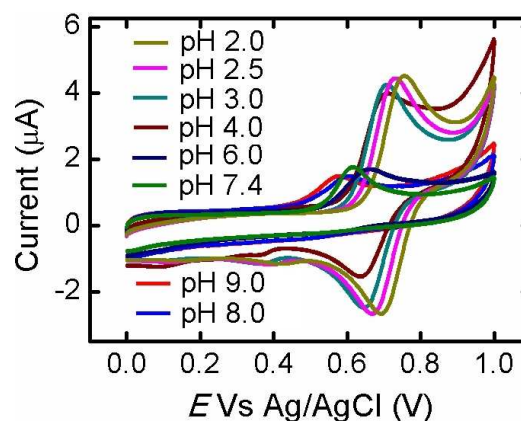

Fig. 5. CVs of a 500 μg/mL KCZ solution in PBS buffer at a scan rate of 100 mV/S on the NDC/GCE under different pH conditions. A 0.1 mg/mL NDC solution was used to make the NDC/GCE.

intensity of the oxidation signal of KCZ increased as the concentration of NDC was increased from 0.05 mg/mL to 0.10 mg/mL, but then plateaued as the concentration of NDC was increased further to 0.20 mg/mL. Therefore, 0.1 mg/mL of NDC was considered to be the optimum concentration for obtaining the best possible electrochemical signal and was used in rest of the experiments. Moreover, the scan rate study of the experimental system as shown in Figure S4 in supporting information ensure the linear dependence of peak current in the calibration plot Figure S4(B) with increasing scan rate, indicating adsorption controlled mechanism [50,51] while electron transport in generating electrochemical signal.

3.5 Electrochemical KCZ Sensor

Figure 6(A) shows CVs of different concentrations of KCZ recorded in PBS buffer (pH 3) at the NDC/GCE. The oxidation peak current increased as the concentration of KCZ was increased from 25 to 500 µg/mL.

Figure 6(B) shows a plot of the oxidation peak current versus KCZ concentration. The NDC/GCE gave a linear response for concentrations of KCZ between 25 and 400 µg/mL (47–752 µM) ($R^2 = 0.9742$). The limit of detection was determined by applying the relation limit of detection = ks/m, where a value of 3 was used for the constant k, and with s defined as the standard deviation of peak current for a zero concentration of ketoconazole and m defined as the slope of the calibration curve used for determining the ketoconazole concentration. Using this method, the detection limit was calculated to be 1.6 µg/mL (3 µM). A comparison of the properties of the currently developed sensor with various previously reported KCZ sensors on modified GCEs is shown in Table S1 in supporting information; this comparison highlighted the practicality of the currently developed sensor. To evaluate technique dependent sensitivity of the developed sensor, a differential pulse voltammetry study has also been carried out for different concentration of

KCZ (Figure S5(A,B) in the supporting information) under same experimental condition and the dynamic range of KCZ was found to be between 25 and 300 µg/mL ($R^2 = 0.96004$) and calculated detection limit was 4.78 µg/mL.

3.6 Real Sample Analysis

The developed NDC/GCE was used for the detection of KCZ from a commercial tablet dissolved in PBS buffer pH 3. The same CV technique was used for detecting KCZ in solutions produced from the tablet as was used for the KCZ solution from Sigma-Aldrich. Four different KCZ tablet solutions were prepared, containing 50 µM, 100 µM, 250 µM and 500 µM of KCZ, respectively. The current signals were plotted in a calibration plot of the obtained real samples for the recovery concentrations of the KCZ from the tablet solution in buffer. Table S2 in supporting information show the experimentally determined recovery and relative standard deviation (RSD) results compared with Figure 6B. The RSD and recovery values obtained were 0.57–4.12 % and 99.2–106 %, respectively. The relatively low (<5 %) RSD values implied high precision levels of the KCZ concentrations determined using the NDC/GCE, and further supported the potential for using this electrode in practical applications.

3.7 Stability, Reproducibility and Selectivity Study

The stability of the NDC-modified sensor was examined by recording CVs of the prepared NDC/GCE before and after storing it at a temperature of 20 °C for 30 days (data not shown). No noteworthy difference between these CVs was observed, indicating the stability of the prepared electrode. The reproducibility of the developed sensor was also evaluated by considering the standard deviation points in the above-described calibration plot (Figure 6 (B)); the reproducibility of the sensor was found to be quite good (relative standard deviation, RSD < 4 %) at
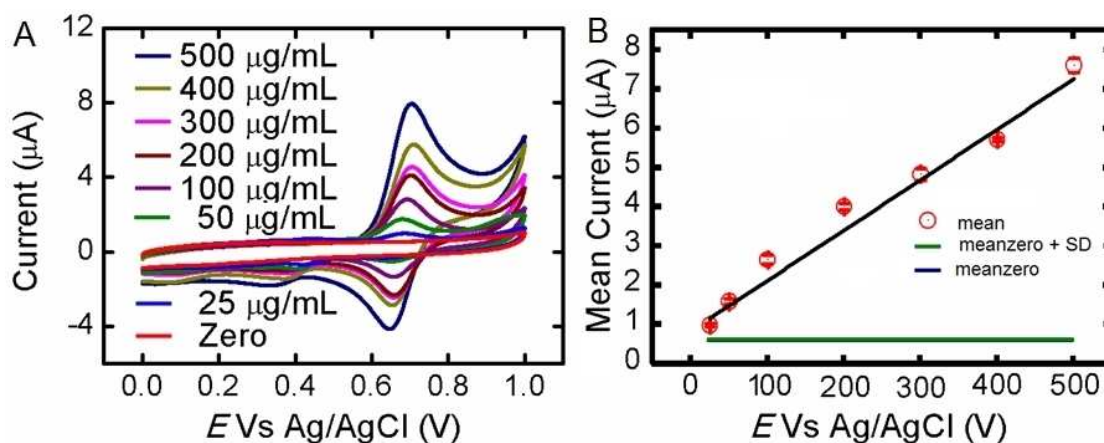

Fig. 6. (A) CVs and (B) corresponding calibration plot for the electrochemical sensing of different concentrations of KCZ in PBS buffer (pH 3.0) using the NDC/GCE.

high concentrations (200 to 500 μg/mL) and reasonable (RSD < 7.5 %) at low (≤ 25 to 100 μg/mL) concentrations. Moreover the selectivity of the sensor has been confirmed by checking CV behavior of all of the six ingredients such as (aerosol 200, maize starch, povidone K30, Lactose monohydrate, magnesium stearate and sodium starch glycolate), which are generally used for ketoconazole drug formulation. It was found in Figure S6 in supporting information that except ketoconazole, all other ingredients except ketoconazole are electroinactive within the potential range of study. The above selectivity study indicates the high selectivity of the developed sensor which is highly appealing.

4 Conclusions

NDC derived from *Clerodendrum Infortunatum* L leaves was concluded to be a cost-effective and efficient electrocatalyst for electrochemical sensors. The developed NDC/GCE-based KCZ sensor was observed to be highly stable and sensitive with reasonable reproducibility. The detection limit (3 μM) obtained using this electrocatalyst was impressive. We expect these results of our study to promote investigations of other porous and doped carbonaceous materials as electrocatalyst alternatives to costly nanomaterials. Importantly, we also expect these results to lead to a crucial role to be played by investigators of tropical countries in the research and development of the health care sector.

Acknowledgement

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