The fabrication of electrochemical sensors for dopamine detection has been attempted with the use of various materials. Metal and metal oxide nanoparticles, enzymes, carbon nanotubes, graphene, ionic liquids, graphene oxide, polymers and some other materials with very high electrocatalytic activity towards biomolecules have served this purpose [7-13]. The synergy between these materials have been harnessed in composites for the manufacture of modifiers for bare conventional electrodes which are ordinarily susceptible to fouling [7]. A wide range of electrochemical sensors made in this fashion have been rewarding in terms of sensitivity and selectivity for dopamine in the presence of interfering molecules but the quest for materials with cheaper precursor and possibly better sensitivity made research in this direction a continuum. Here in, the determination of dopamine with copper oxide nanoparticles (CuO NPs) and CQDs nanocomposite has been attempted. This was inspired by the low band gap and the attendant high electrical conductivity of CuO NPs. The CuO NPs was prepared via chemical precipitation technique and incorporated into a composite with CQDs prepared from the carbonization of pencil graphite. The resultant composite was used for the modification of glassy carbon electrode for the fabrication of the sensor used in this study.

Graphitic carbon dot/copper oxide nanocomposite based electrochemical sensor for dopamine detection

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ABSTRACT

The present work presents the synthesis of graphitic carbon dot (CQDs) and copper oxide (CuO) nanomaterials via the chemical oxidation and co-precipitation techniques, respectively. These materials and their composite (CQDs/CuO) were characterized using the FT-IR, UV-vis, EDS, SEM, TEM and XRD prior to modification with glassy carbon electrode. The electroanalysis of dopamine at the GCE/CQDs/CuO modified electrode gave a limit of detection of 25.4 μM over a concentration linear range of 1-180 μM. The application of this sensor for DA detection in the presence of ascorbic acid (AA) was also investigated. The sensor gave a wide AA-DA peak separation, suggesting no interference of the (AA) peak with DA peak. The sensor also exhibited good reproducibility and recovery of the analyte from dopamine hydrochloride detection.

Keywords: Graphitic carbon dot, copper oxide, dopamine, glassy carbon electrode, square wave voltammetry

INTRODUCTION

Dopamine is about the most studied neurotransmitter (NT). This could be attributed to its significance as a NT with the capacity to coordinate essential activities of the entire human system such as learning, behavior, emotion and movement [1]. By implication, the imbalance in the concentration of this biomolecule has been implicated in chronic diseases like Parkinson's disease, dementia, epilepsy, schizophrenia among others [2,3]. Spectrophotometry [4], chromatography [5], capillary electrophoresis [6] and electroanalytical methods [6,7] are the analytical techniques that have been deployed for the detection of this analyte. The ease of handling, cost-effectiveness, selectivity and sensitivity of the electrochemical sensors informed the preference of this electroanalytical method by scientists relative to other analytical means which hardly combine all of these attributes [7].

The fabrication of electrochemical sensors for dopamine detection has been attempted with the use of various materials. Metal and metal oxide nanoparticles, enzymes, carbon nanotubes, graphene, ionic liquids, graphene oxide, polymers and some other materials with very high electrocatalytic activity towards biomolecules have served this purpose [7-13]. The synergy between these materials have been harnessed in composites for the manufacture of modifiers for bare conventional electrodes which are ordinarily susceptible to fouling [7]. A wide range of electrochemical sensors made in this fashion have been rewarding in terms of sensitivity and selectivity for dopamine in the presence of interfering molecules but the quest for materials with cheaper precursor and possibly better sensitivity made research in this direction a continuum. Here in, the determination of dopamine with copper oxide nanoparticles (CuO NPs) and CQDs nanocomposite has been attempted. This was inspired by the low band gap and the attendant high electrical conductivity of CuO NPs. The CuO NPs was prepared via chemical precipitation technique and incorporated into a composite with CQDs prepared from the carbonization of pencil graphite. The resultant composite was used for the modification of glassy carbon electrode for the fabrication of the sensor used in this study.

MATERIALS AND METHODS

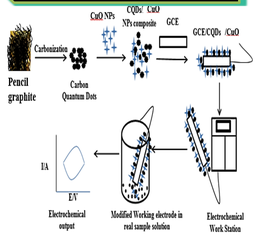
All chemicals were supplied by Sigma Aldrich Chemicals, Pomona AH, Kempton Park, 1619, South-Africa. All reagents were of analytical grade. HB pencils were procured from *shop rite*, mega city mall, Mmabatho, South-Africa.

The UV-visible spectroscopy was done with Uviline 94000 UV spectrophotometer (with wavelength range of 200-700 nm) supplied by SI analytics, Germany. Scanning electron microscopy (SEM) was done with Quanta FEG 250 microscope supplied by ThermoFisher Scientific, USA. Prior sample preparation in ethanol and subsequent deposition on a solid substrate (mica) were done before SEM analysis

The functional groups in the materials were analysed with Fourier-transform infrared (FT-IR) spectrophotometer procured from Brucker Corporation, USA. The FT-IR spectrophotometer (Opus Alpha-P) was applied within a wavelength range of 400-4000 nm. X-ray diffractograms were obtained with Rontgen PW3040/60 X'Pert Pro diffractometer at 2° min^{-1} scan rate and diffraction angle of 10° - 90°

All electrochemical measurements were done using an Autolab potentiostat/galvanostat PGSAT-20 operating on Nova 1.3 software and an electrochemical cell with a three electrode system. The reference, working and [illegible] GCE,

EXPERIMENTAL



RESULTS

Spectroscopic characterization

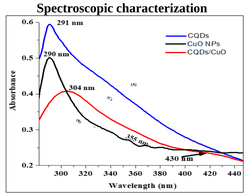


Fig. 1: UV spectra of (A) CQDs (B) CuO nanoparticles (C) CQDs/CuO nanocomposite

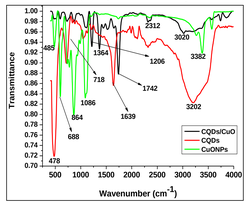


Fig. 2: FT-IR spectra of CuO nanoparticles, CQDs and CQD/CuO nanocomposite

Electrochemical characterization of modified electrode

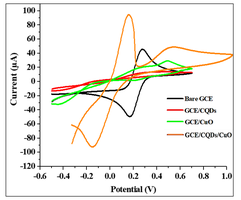


Fig. 5: Cyclic volatmmogram of bare GCE, GCE/CQDs, GCE/CuO and GCE/CQDs/CuO in 10 mM $[Fe(CN)_6]^{3-/4-}$ redox probe in PBS (pH 7.0) at a scan rate of 25 mV s^{-1}

Interference study

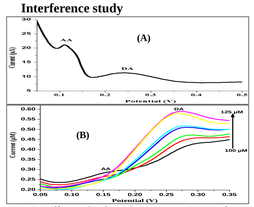


Fig. 9. Differential pulse voltammogram (DPV) of DA in the presence of AA. DPV of AA in the presence of varying DA concentration.

RESULTS - CON'T

Morphological characterization

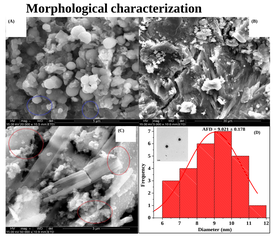


Fig. 3: SEM micrograph of (A) CuO nanoparticles (B) CQDs (C) CQDs/CuO nanocomposite and (D) particle size distribution chart from the TEM micrograph of CQDs

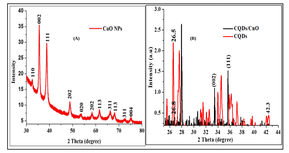


Fig. 4: XRD diffractogram of (A) CuO NPs and (B) CQDs and (C) CQDs/CuO

Electrocatalysis at modified GC electrode

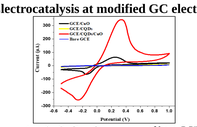


Fig. 6: Cyclic voltammogram of bare GCE, GCE/CQDs, GCE/CuO and GCE/CQDs/CuO in 0.4 mM DA in PBS (pH 7.0) at a scan rate of 25 mV s^{-1}

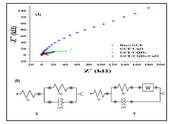


Fig. 7: EIS spectrum (Nyquist plot) and equivalent circuit of the bare and modified electrodes in 0.4 mM DA in PBS (7) at a scan rate of 25 mV s^{-1}

Effect of scan rate

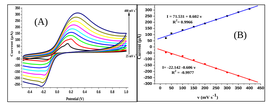


Fig. 8: Cyclic voltammogram showing the effect of scan rate on DA peak current at GCE-CQDs/CuO modified electrode. (B) Plot of Current against scan rate.

RESULTS - CON'T

Table 1: LoD and LDR of nanocomposite modified electrode

Electrode	LoD (μM)	LDR (μM)
GCE/CQDs/CuO	25.4	10 -180

Table 2: Real sample analysis data (n=3)

Amount added (μM)	Amount Found (μM)	Recovery (%)
50	46.524	93
50	50.98	102
50	45.098	90.2

DISCUSSION

The synthesis and characterization of CQDs, CuO NPS and their composite was achieved in this study. The UV spectrum (Fig. 1) , FT-IR spectrum (Fig. 2) XRD diffractogram (Fig. 4) and the morphological characterization with scanning electron microscopy (SEM) (Fig. 3) confirmed the successful synthesis of these materials. The average particle size of the CQDs (9.02 nm) is similar to the < 10 nm reported for quantum dots [14]. The modification of bare GCE with these materials for electrochemical detection of dopamine and the electrochemical characterization in $[Fe(CN_6)]^{3-/4-}$ redox probe shows that the CQDs/CuO modified GCE has a superior catalytic effect (Fig. 5). This same modified electrode offered the best electrocatalytic effect on the oxidation of dopamine compared to other modified electrodes (Fig. 6). The charge transfer resistance of this electrode (Rct) as obtained from the EIS spectra of the modified electrodes (Fig. confirms that the CQDs/CuO modified GCE possess the lowest Rct (Fig. 7A). The equivalent circuit X represent that of the GCE/CQDs/CuO while other electrodes were modelled with Y (Fig. 7B). Figure 8 A shows the changes in current response with scan rate changes. The peak current response increased with increase in scan rate following the linear relationship seen in Figure 8 B. This relationship suggest that the oxidation of dopamine at GCE/CQDs/CuO is a surface confined process. The cyclic voltammograms also show that DA oxidation is a quasi-reversible process. The interference of ascorbic acid (AA) with dopamine (DA) was investigated using the differential pulse voltammetry (DPV), Figure 9 A shows the resolution of the AA-DA peak. Figure 9 B shows that the AA signal did not interfere with DA with every increase in DA concentration (100-126 μM) while AA concentration remain constant (1 mM). This sensor offered a detection limit (LoD) of 25.4 μM over a linear dynamic range (LDR) of 10-180 μM (Table 1). The sensor was also applied for the detection of dopamine in dopamine hydrochloride injection with a percentage recovery of 95 % (n=3) and a percentage relative standard deviation (% RSD) of 6.5 %. Table 2 shows the data obtained for this real sample analysis.

Conclusions

In this study, we reported a sensor based on CQDs and CuO NPs nanocomposite for dopamine detection. The sensor shows a promising application for accurate dopamine detection considering its LOD and the relatively wide linear range it possesses. In addition, the good recovery obtained from the application of this sensor for dopamine detection in dopamine hydrochloride injection suggest that this sensor is suitable for the detection of dopamine in pharmaceutical samples. The figures of merit of this sensor such as its low LoD, wide LDR and the good recovery obtained in DA hydrochloride injection are indications that the sensor can be commercialized for a point-of-care dopamine detection in pharmaceutical samples down to the micromolar level.

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Acknowledgements

This project was supported by the Department of Chemistry, Faculty of Natural and Agricultural Sciences, North-West University (Mafikeng Campus). SEE and OEF acknowledge the Department of Chemistry, Faculty of Natural and Agricultural Sciences, North-West University (Mafikeng Campus) for the support during the course of this project.

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