In recent years, selective and sensitive detection of bio-molecules using various selective nanomaterials have been received more attention due to their high conductivity, surface energy and favorable interaction with other molecules. 

Electrochemical sensors for assaying bio-molecules offers several unprecedented advantages over the conventional methods (For examples, Fluorescence methods, chromatography techniques, UV-vis, etc.) such as highly sensitive and selective detection, goes up to femto level detection, easy to handle, reduces manual errors, suitable for field analysis and can be automated. 

The electrochemical sensors have already been used to detect biological molecules, volatile gases (hazardous to humans and environment), analyzing the thermal condition and contamination in food samples.

Another use for electrochemical sensors is to detect molecules produced in the human body. Dopamine ([4-(2-aminoethyl) benzene-1,2-diyl] (DA) is one of the catecholamine (neurotransmitter) present in the central nervous system. Various catecholamines secreted in the body and their concentration levels are very important. More specifically, if the concentration level of DA slightly change, it could affect the brain functions and impact learning and listening processes. DA’s role is to send the signal from one nerve cell to another cell including the brain pathway. The abnormal secretion level of DA could affect the brain functions and impact learning and listening processes. The abnormal secretion level of DA may lead to Parkinson disease, schizophrenia, bipolar disorder, depression, etc.

So, the detection of DA in biological sample is crucial since it plays a vital role in our body.

Past DA determination research included photoluminescence quenching method using silica nanoparticles, chemiluminescence, capillary electrophoresis, colorimetry and high performance liquid chromatography. These methods each have their limitations. For example, they required sample pre-concentration, longer analysis time, skilled person, expensive equipment’s etc. 

Therefore, electrochemical sensors are more attractive. Prevalently, modified electrodes have been reported to detect dopamine in different detection range. Unfortunately, the selectivity of the sensor is dependent on the presence of ascorbic acid (AA) and uric acid (UA) which co-exist in the body with concentrations much higher than that of DA. In addition, they interfere in electro-analysis of DA because of their overlapping electro-oxidation potentials (DA, AA and UA). Oxidation of DA will catalyze the oxidation of AA. Kumar et al. reported a method for the detection of DA and AA with a detection limit of 0.1 μM for DA and 1 μM for AA. Huang et al. reported a palladium nanoparticles/carbon nanofiber modified carbon paste electrode for simultaneous detection of DA, AA and UA by using differential pulse voltammetry. Li et al. detected DA, AA and UA using a GCE modified with polyvinyl alcohol and their individuals oxidation peaks were obtained. Lian et al. have also reported a method for the detection of AA and DA using graphene/tryptophan modified electrode from 0.5 to 110 μM. Similarly, other DA sensors were reported using graphene, carbon nanotube and nitrogen doped carbon quantum dot (CQD).

CQD has the fluorescence behavior and has been utilized in various research fields such as photo-catalyst, bio-imaging, electrical chemiluminescence etc. Unique advantage of CQD is that it has high active surface area due to their small size which is less than 10 nm. In addition, CQD has exhibited good electronic, optical and electrical properties. The synthesis of CQD was reported by laser ablation of graphite, microwave synthesis, bottom up methods, electrochemical oxidation of graphene oxide and from natural sources like sugarcane, orange peel, Borassus flabellifer flowers and corn. But, these synthetic methods need very high temperature, extensive acid usage and could generate more chemical waste etc. Among these methods, electrochemical exfoliation of graphite to CQD is considered as a green method, does not take as long to do, and can be performed at room temperature with high product yield.

In this study, electrochemical synthesis of CQD is reported by using graphite rod as anode and cathode, respectively. The as-synthesized CQD particle sizes were measured by high-resolution transmission electron microscopy (HR-TEM) and UV-Visible spectroscopy (UV-Vis). Then, CQD dispersion was used to modify screen printed carbon electrode (SPCE with in-built three electrode configuration) and GCE. Compared to traditional solid electrodes, disposable SPCE’s offers several advantages such as low sample volume, flexible operating temperature, and low cost.

In the following work, we have...
used SPCE and CQD for a DA sensor. The CQD modified electrodes, electrochemical and electro-catalytic properties were assessed. The linear range of DA detection was from 1 to 7 μM on SPCE/CQD. The effect of interference was also studied after coating with Nafion (NF) on the CQD modified electrode. The SPCE/CQD modified electrode was also applied to and detect spiked DA in human urine samples.

Experimental

Chemicals and reagents.— Sodium hydroxide (NaOH), AA and DA were purchased from Sigma-Aldrich, India. Graphite rod was from Graphitestore.com, Inc., IL, US. Ethanol (99.9%) was purchased from analytical reagent, Changshu Hong sheng Fine Chemicals Co. Ltd. Potassium monohydrogen phosphate (K₂HPO₄) and potassium dihydrogen phosphate (KH₂PO₄) were purchased from Alfa Aesar. The SPCE’s (in-built three electrode configuration, working electrode with 3 mm diameter) were purchased from Zensor. GCE was purchased from CH Instruments, USA. The standard solutions were prepared using milli-Q water. The electrolyte solution was 0.1 M PBS (pH 7.4) which was prepared by using K₂HPO₄ and KH₂PO₄ in aqueous media.

Apparatus and equipment.— The electrochemical measurements were done by an electrochemical workstation from CH Instruments, USA (Model: CHI-760E). The surface morphology of CQD and their size range was analyzed by HR-TEM-2100 Plus Electron microscope (JEOL, Japan). The UV-visible spectra were recorded using 2000c nanodrop spectrophotometer, Nanodrop technologies, USA. DC power supply (Model: 2231A-30-3 triple channel DC power supply from Keithley a Tektronix company, USA) was used for electrochemical exfoliation of graphite. CQD were characterized by using Fourier-transform infrared spectrometer (FT-IR) (FT-IR-NICOLET 380) and X-ray diffraction spectrometer (XRD) (XRD-PA analytical XpertPro).

Preparation of CQD.— The electrochemical preparation of CQD was carried out as follows: Two individual Graphite rods (width ~ 0.2 cm) were used as the cathode and anode in the alkaline solution (0.1 M NaOH/ethanol (EtOH)/water as the electrolyte. Length of both rods was 5 cm long and about 1 cm of electrodes were immersed into the solution to carry out the reaction. A constant current of 50 mA was applied using a DC power supply. The electrochemical exfoliation was started at the anode and the different sizes of CQDs were generated by the electrochemical cutting of graphite surface. The mechanism of CQD synthesis could be described as follows. The electrolyte solution containing 0.1 M NaOH/EtOH which formed sodium salt of ethanol (C₂H₅ONa) and the hydroxide (OH⁻) ions. The free OH⁻ ions were attracted to the anode instigating oxidation, which lead to the electrochemical cutting of graphite as it produced CQD. Finally, the color of the solution was changed from colorless to light yellowish red and then became dark red solution within 3 hr. After that, this solution was water bath sonicated for 30 min and then filtered using a Whatman filter paper (0.22 μm). A clear red solution was obtained and stored for further analysis in the refrigerator at 4°C (Fig. 1). The CQD was stable up to three days without any aggregation.

The control experiments were also conducted in aqueous medium without EtOH. It undergoes hydrolysis of water with strong exothermic reaction to produce hydrogen gas, but it did not form the CQD. In another experiment, the exfoliation reaction was tried with only EtOH, after that 3 μL of DA oxidation was studied in 0.1 M PBS. To detect DA in the presence of AA, 10 μL Nafion (NF) (0.125% W/V) solution was placed on the CQD film and formed a layer to avoid the interference effect in 0.1 M PBS.

Results and Discussion

Characterization of CQD materials.— Fig. 1 shows the electrochemical synthesis of CQD in alcoholic NaOH at different time intervals. The electrolyte color changes from colorless to light yellowish red (in 1 hr) and then finally turns to deep red. It represents the successful synthesis of different particle sizes as it confirmed by UV-Vis spectra (Figs. 2a–2c). The obtained CQD (red) dispersion was bath sonicated for 30 min and then filtered through a Whatman filter paper (~0.22 μm). Then, CQD dispersion was analyzed by UV-Vis (Figs. 2a–2c). Fig. 2a (inset) shows the green fluorescence emission of CQD under UV light at the wavelength of 365 nm. The UV-Vis spectra were recorded by using EtOH as a reference solution. As-prepared CQD dispersion (after filtration) showed an absorption peak around 250–300 nm corresponds to π-π*conjugation of aromatic system of CQD (Fig. 2a). The broad absorption bands observed from 250 to 400 nm indicated the presence of different particle sizes. The GCE and SPCE were coated by 10 μL CQD dispersion via drop casting method and dried in the room temperature for 10 min. After complete dry, it was washed with de-ionized (DI) water and again dried. Then, the SPCE/CQD or GCE/CQD modified electrode was cyclized from −0.2 to 0.6 V at a scan rate of 50 mV/s in 0.1 M PBS solution. Furthermore, cyclic voltammograms (CVs) were recorded before and after each addition of DA using SPCE/CQD as a working electrode. Ag/AgCl and platinum were used as the reference and counter electrode. The corresponding oxidation and reduction peak potentials of DA were recorded. The effect of scan rate on 3 μM DA oxidation was studied in 0.1 M PBS. To detect DA in the presence of AA, 10 μL Nafion (NF) (0.125% W/V) solution was placed on the CQD film and formed a layer to avoid the interference effect in 0.1 M PBS.

Effect of time on synthesis of CQD.— Electrochemical exfoliation progress was monitored by analyzing the samples taken out from the reaction mixture after 0 min, 5 min, 10 min, 30 min, 1 hr, 2 hr, and 3 hr intervals at a constant current of 50 mA (Figs. 2b and 2c). The UV-Vis spectrum of sample obtained after 5 min of exfoliation showed an absorption peak at ~270 nm. But, with the time increases, the absorption peak intensity was also increased. After 15 min, another broad absorption peak was started to appear at 360 nm. From this study, it was confirmed that with the time, the exfoliation of CQD resulted in various particle sizes (Fig. 2c). The UV-Vis spectra of these samples were recorded without filtration (Fig. 2c), that was the reason for differences observed in the UV-Vis spectra between Figs. 2a and 2c. However, the major absorption bands were observed similarly in both spectrums which confirmed the formation of CQD (Figs. 2a and 2c).

TEM, XRD and FT-IR analysis.— The CQD surface morphology and the size were characterized by HR-TEM. CQD sample was diluted with EtOH, after that 3 μL of CQD was coated on the copper grid and dried at the room temperature for 24 hr. Using this sample, the
Figure 2. (a) UV-Visible spectrum of the synthesized CQD dispersion after filtration process. (b and c) Effect of time on synthesis of CQD from 0 to 3 hr (i to vii) at 50 mA in 0.1 M NaOH/EtOH solution using graphite rods as electrodes (note: UV-Vis was recorded without filtration). (d and e) The HR-TEM images of the CQD particles.

average particle sizes of CQD were found to be ∼7 nm (Figs. 2d, 2e).\textsuperscript{40} Fig. 3a shows the XRD data of graphite and synthesized CQD material. The exfoliated CQD had a broader peak appeared at 24.3° which indicated the formation of zero-dimensional material from graphite rod. The graphite rod showed a sharp peak at around at 25.76, which later shifted to 24.3 due to changes in interlayer distance in CQD compared to graphite material.\textsuperscript{38} The interlayer distance was also calculated using Bragg’s equation which was higher for CQD materials (0.40 nm) due to the presence of more oxygen functional groups. These functional groups were introduced during the exfoliation process, and it had the amorphous nature than the graphite (0.13 nm).\textsuperscript{31} Fig. 3b shows the FT-IR spectrum of CQD. An absorption peak observed around at 3400 cm\(^{-1}\) corresponds to the acid functional group present on the CQD surface (such as -COOH, -OH), respectively. FT-IR also confirmed presence of carbonyl group on CQD by a strong absorption peak at 1645 cm\(^{-1}\). In addition, the peak observed at 2100 cm\(^{-1}\)corresponds to C-C multiple bonds of CQD (Fig. 3b).\textsuperscript{42} These results successfully indicated that functionalized CQD were produced by the electrochemical exfoliation method.

Electrochemical oxidation of DA.—In order to test the electrocatalytic activity of the CQD, we modified SPCE and GCE as described in section DA sensor fabrication. Fig. 4a shows the CVs of the GCE/CQD modified electrode in the presence of 10 μM DA in 0.1 M PBS. A highly reversible redox peak with oxidation and reduction potentials were observed at 0.22 and 0.09 V, respectively (Fig. 4a, curve ii).\textsuperscript{43} When compared with the bare-GCE (curve i), CQD coated electrode enhanced the DA oxidation and reduction currents with good reversibility, and current intensity increased by 13% which indicated the electrocatalytic activity of CQD film (Fig. 4a). In the same manner, SPCE was also modified and tested with 3 μM DA. It also showed a high catalytic current for DA oxidation at 0.24 and reduction at 0.2 V (Fig. 4b). This study successfully confirmed that CQD modified electrode had good electrocatalytic activity for DA in 0.1 M PBS.

Effect of scan rate.—The effect of scan rate on the electrochemical oxidation of DA (3 μM) was studied at the SPCE/CQD from 10 mV to 150 mV/s. It showed a linear response for \(I_{pa}\) vs. scan rate at 0.24 V. This phenomenon indicated the surface-controlled electrode reaction.
Figure 3. (a) XRD and (b) FT-IR spectrum of as-synthesized CQD.

Figure 4. (a) CVs of 10 μM DA in 0.1 M PBS at (i) bare GCE and (ii) GCE/CQD (Scan rate = 50 mV/s). (b) The SPCE/CQD modified with 3 μM DA in 0.1 M PBS. (c) The effect of scan rate on $I_{pa}$ and $I_{pc}$ of 3 μM DA at SPCE/CQD. (d) The plot shows the linear relationship between scan rate vs. $I_{pa}$ and $I_{pc}$ on 3 μM DA.
of DA at the SPCE/CQD (Fig. 4c). A linear regression equation was fitted for different scan rate vs. \( I_{pa} \) (anodic peak current) which found to be \( I = 0.008x + 0.105 \) (\( r^2 = 0.99 \)) and \( I = 0.006x + 0.115 \) (\( r^2 = 0.992 \)) for \( I_{pc} \) (cathodic peak current) of DA (Fig. 4d).

**Calibration graph of DA.**—Fig. 5a shows CVs of a SPCE/CQD modified electrode in PBS with different concentration of DA. With each successive additions of DA from 1 to 7 \( \mu \)M, the oxidation peak currents increased linearly at 0.24 V with respect to the DA concentration. The oxidation potential of DA slightly shifted toward the positive side because the diffusion process is controlled and the mass transfer becomes difficult, when DA concentration gradually increased, so the electrochemical system applies more potential and shifted the oxidation potential of DA toward positive side (Fig. 5a). After that, it reached a saturation point and did not respond linearly. A calibration graph was recorded using the \( I_{pa} \) vs. the concentration of DA which was linear with an equation of \( y = -0.069x - 0.436 \) (\( r^2 = 0.98 \)). The detection limit of DA was estimated to be 0.099 \( \mu \)M (S/N = 3) (Fig. 5b).

**Mechanism of DA electrochemical oxidation.**—The electrooxidation of DA on CQD film modified electrode might follow as given below: DA molecules were first get oxidized by leaving two electrons to become dopamine quinone. Then, it undergoes a cyclization reaction to yield leucodopaminochrome (LDC) by intramolecular 1,4-Michael addition arrangement. LDC was more reactive than the parent DA which oxidizes easily to dopaminechrome (DC) (Scheme 1). The enhanced electro-catalytic activity of the CQD might come from its negatively charged functional groups such as OH-, COO-, etc. The pKa of DA is 8.9, so it was positively charged in 0.1 M PBS (pH 7.4) which might attracted to the negatively charged CQD film modified electrode.

**Interference studies, reproducibility and real sample analysis.**—We recorded CVs for 10 \( \mu \)M DA in the absence and presence of 1 mM AA as shown in Fig. 6. In order to avoid the interference problem, 10 \( \mu \)L Nafion (Nf) (0.125% W/V) dispersion was placed and dried on the GCE/CQD modified electrode (note: loosely bounded Nf was removed by washing in distilled water). Next, CVs were recorded in 0.1 M PBS with 10 \( \mu \)M DA. GCE/CQD/Nf showed an oxidation peak at 0.22 V and reduction peak at 0.09 V. However, after the addition of 1 mM AA into 0.1 M PBS with 10 \( \mu \)M DA, the redox reaction to yield leucodopaminochrome (LDC) by intramolecular 1,4-Michael addition arrangement. LDC was more reactive than the parent DA which oxidizes easily to dopaminechrome (DC) (Scheme 1). The enhanced electro-catalytic activity of the CQD might come from its negatively charged functional groups such as OH-, COO-, etc. The pKa of DA is 8.9, so it was positively charged in 0.1 M PBS (pH 7.4) which might attracted to the negatively charged CQD film modified electrode.

**Scheme 1.** Mechanism of electrochemical oxidation of DA on SPCE/CQD film modified electrode.

**Figure 6.** CVs were recorded using a GCE/CQD/Nf in 0.1 M PBS containing 10 \( \mu \)M DA in the absence and presence of 1 mM AA. Scan rate = 50 mV/s.
Table I. Comparison of linear range, LOD, the modifier material and method used for DA detection.

| S. No. | Materials/electrode used           | Method      | Linear range | LOD      | Reference |
|--------|------------------------------------|-------------|--------------|----------|-----------|
| 1      | Graphene/GCE                        | CV          | 4–100 μM     | 2.64 μM | 49        |
| 2      | Polyvinyl alcohol/GCE               | CV/DPV      | 0.5–30 μM    | 0.018 μM| 21        |
| 3      | Tryptophan-Graphene/GCE             | CV/DPV      | 0.5–110 μM   | 0.29 μM | 9         |
| 4      | Porous graphene oxide/gold nanoparticle | CV/amperometry | 0.1–30 μM    | 1.28 μM | 51        |
| 5      | LaMnO₃                             | CV/DPV      | 1–100 μM     | 6.22 μM | 52        |
| 6      | Screen printed graphene             | DPV         | 0.5–2000 μM  | 0.12 μM | 50        |
| 7      | CQD-SPCE                           | CV          | 1–7 μM       | 0.099 μM| This work |

peak of DA was not affected. The DA oxidation and reduction peaks were observed without any change in redox peak currents, but with a small shift in oxidation peak to 0.20V. It confirmed that the adlayer of Nf was blocked the AA from reaching the electrode surface.

We propose that by using GCE/CQD/Nf or SPCE/CQD/Nf modified electrode, it is possible to detect selectively DA in the presence of AA.

Reproducibility of the sensor for DA detection was also performed by repeating analysis of 10 μM DA by using three different individually modified electrodes. The standard deviation (s) was 0.514. It showed that our electrode modification procedure is reproducible. We also compared the linear range and limit of detection (LOD) of our method with other reported methods in Table I. As can be seen, the linear range, and LOD of the present method were comparable to those reported by others using graphene, polyvinyl alcohol, tryptophan/graphene, porous graphene oxide/gold nanoparticles, LaMnO₃ and graphene/SPCE modified electrodes.

The real-world application of our sensor (SPCE/CQD) was also tested in human urine samples spiked with known concentration of (3 μM) DA. For this analysis, CVs were recorded in 0.1 M PBS with the addition of various concentrations of diluted urine samples. Urine samples of 100, 200 and 300 μL were added to the standard concentration (3 μM) of DA and CVs were recorded as shown in Figs. 7a–7c. As can be seen, DA oxidation peak current was observed without any obvious changes in the presence of various concentration of urine samples. This is the proof that DA detection can be performed in real samples using SPCE/CQD film modified electrode (Table II). The obtained DA concentration were reliable and in the range of acceptable levels. The DA recovery was in the range from 102 to 105% (Table II).

Figure 7. CVs were recorded in 0.1 M PBS with different concentrations (a) 100 μL, (b) 200 μL, and (c) 300 μL urine samples (human urine) with 3 μM DA at a SPCE/CQD, scan rate = 50 mV/s.
from 1 to 7 µM at SPCE/CQD modified electrode. The real sample analysis was performed to detect DA in human urine samples which showed acceptable recovery values. We see potential for this electrochemical method of CQD synthesis and the SPCE/CQD modified electrode for various future application.

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