Graphene-conductive polymer-based electrochemical sensor for dopamine detection

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ABSTRACT

The central nervous system’s (CNS) dopaminergic system dysfunction has been linked to neurological illnesses like schizophrenia and Parkinson’s disease. As a result, sensitive and selective detection of dopamine is critical for the early diagnosis of illnesses associated with aberrant dopamine levels. In this research, we have investigated the performance of electrochemical screen-printed sensors for different concentrations of dopamine detection using graphene-based conductive PEDOT: PSS(G-PEDOT: PSS) and Polyaniline(G-PANI) inks on the working electrode and compared the sensitivity. SEM characterization technique has been performed to visualize the microstructures of the proposed inks. We have investigated cyclic voltammetry (CV) electrochemical techniques with ferri/ferrocyanide redox couple to assess the efficiency of the designed electrodes in detecting dopamine. G-PANI ink has shown to have better LOD and stability to detect dopamine with screen-printed electrodes. Further, we have also studied electrochemical analysis for the selective detection of dopamine without the interference of Ascorbic Acid (AA).

1. INTRODUCTION

Dopamine (3,4-dihydroxy phenyl)ethylamine, DA) is one of the most important and researched catecholamine neurotransmitters as it acts as an extracellular messenger and plays an important role in the effective function of human metabolism, cardiovascular, central nervous, renal, and hormonal systems. Low DA concentration is an indicator of Parkinson’s disease, depression, and DA transporter deficiency syndrome, while a higher concentration of dopamine is deeply related to obesity, addiction, and schizophrenia. In the "caudate nucleus," an area of the brain, DA concentrations can reach the micromolar range[1]. Drugs of abuse, such as cocaine and amphetamines, can block the mechanism of collecting DA from the surrounding fluid, resulting in the behavioral alterations that these drugs cause. Monitoring DA neurotransmission directly can provide new insights into this mechanism, to design therapeutics for DA-related disorders[2]. As a result, designing and developing a quick, sensitive, and selective physiologic DA concentration measurement system is critical.

There have been numerous methods developed and used for DA detection, including high-performance liquid chromatography (HPLC)[3], Surface Plasmon Resonance (SPR)[4], colorimetry[5], chemiluminescence[6], spectroscopy. Despite being exact and sensitive, these approaches require complex and advanced instrumentations, as well as a significant amount of time to complete. Chemical modification, rather than biological substrates, is generally more useful in the detection of DA. Methods based on electrochemistry provide a highly sensitive technique for the detection of a diverse variety of analytes and are popular because they are easy to use, quick to perform, may be done online, and provide a highly sensitive method of detection[7]. DA being easily oxidizable, electrochemical methods based on anodic oxidation are appropriate for quantifying DA[8].

Through several primary stages, an electrochemical sensor is capable of converting an electrical output signal to a digital signal for further analysis. In general, electrochemical sensors provide a response as a result of the interaction of chemistry and electricity, as determined by potentiometric, amperometry, and conductivity measurements. Among various electrochemical techniques, CV is one of the most popular methods for being rapid and inexpensive.

An exchange of two electrons and two protons takes place in the DA compound when a voltage is supplied to the electrode resulting in the DA compound being subsequently oxidized to become cytotoxic dopamine quinone (DAQ). Direct detection of DA without surface modification suffers from the problems of weak signal, low electron transfer rate[9], and fouling effect[10]. Thus, surface modification of the working electrode is an effective method of resolving these issues by achieving an appropriate change in order to gain high sensitivity and selectivity toward DA sensors[11].

The chemically modified electrodes are often made with active materials and metal nanoparticles (Au, Ag, Pt, Pd, Cu)[12-15] metal oxides (TiOx, Fe2O3, CuO, ZnO, Fe3O4)[16-18] polymers (Naion, chitosan, o-phenylenediamine, polyaniline, polypyrrole) carbon nanotubes, zeolite, [19] and clay.

Recently, Graphene research has advanced one step forward by demonstrating graphene’s potential to act as a robust and...
conductive filler for polymer matrix to build graphene-based polymer composites. Conductive Polymers coupled with graphene exhibit better conductivity, tunable surface property, superior biocompatibility, and stability. Moreover, the combination of graphene with conductive polymers improves graphene's optical, electrical, and mechanical capabilities. PEDOT:PSS (poly(3,4-ethylenedioxythiophene) polystyrene sulfonate) incorporated in graphene tremendously improves solubility in aqueous solutions and shows improved conductivity and stability. Polyaniline (PANI) also has significant conductivity, stability, and redox behaviour.

For DA detection, numerous examples are given in the literature including pre-treated electrodes[20], self-assembled monolayer modified electrodes[21], covalent modification[22], polymer film[23], composite electrodes[24], and screen-printed electrodes[20]. Screen-printed electrode offers advantages over traditional electrodes, including being inexpensive, reliable, quicker, easy to use and environmentally friendly.

Jing Zou et al. have proposed two-dimensional (2D) g-C3N4/CuO nanocomposites for the ultrasensitive detection of DA[25]. Mehmet Senel et al. have developed a microfluidic electrochemical sensor for monitoring DA levels in cerebrospinal fluid and plasma of a mouse model of PD[26]. Derric Butler et al. have introduced a post-deposition annealing process for increasing the sensitivity of commercial graphene ink to detect DA[27]. Synthesized polysaccharide-based carbon quantum dots (CQDs) have been proposed by Guangda Han et al. for the highly selective detection of DA[28]. In our work, we have developed graphene-conductive based polymer inks by utilizing some simple steps and used commercially available screen-printed electrodes as a sensor platform. In the future, we would modify our proposed inks for the detection of dopamine in human blood and urine sample.

In this paper, we have developed graphene conductive polymer PEDOT: PSS and Polyaniline based ink respectively and compared the performance of the ink for DA detection with screen-printed carbon electrodes. Graphene conductive based Polyaniline ink provides better results in detecting DA.

2. MATERIALS AND METHODS

2.1 Materials

All the chemicals have been bought from Sigma-Aldrich.

2.2 Experimental Procedures

Graphene conductive PEDOT:PSS ink is made of 1 gm Graphene nanoflakes, 0.1 gm PEDOT:PSS, 800 µL DMSO and 6ml DI water. Due to the substantially low conductivity of PEDOT:PSS (1 S/cm) and the hydrophilicity of PSS, DMSO has been used to increase conductivity[29]. Graphene conductive Polyaniline ink is composed of 1gm Graphene nanoflakes with 2 mL Polyaniline, 4 mL phytic acid and 6 mL DI water. These chemicals are mixed with planetary Hauschild SpeedMixer SMART DAC 250 for making a homogenous ink solution. The Planetary mixer has a mixing capacity of up to 250 gm, and the mixing speed range is 300 to 2500 RPMs. The experiments are conducted at room temperature and normal atmospheric pressure.

Around 2 µL inks are deposited on a screen-printed working electrode with a micropipette and left for 24 hours. Autolab Potentiostat has been used to perform electrochemical cyclic voltammetry experiments. The voltage range is -0.5 V to 0.35 V with a scan rate of 0.08 V/sec, and the upper current range was 10 mA, and the lower current range was 10 µA.

3. RESULTS AND DISCUSSION

3.1 Characterization of G-PEDOT:PSS and G-PANI ink

Figure 1 depicts SEM images of Graphene conductive PEDOT:PSS (G-PEDOT:PSS), and figure 2 shows SEM images of Graphene conductive Polyaniline ink (G-PANI).
Figure 1: SEM characterization images of G-PEDOT:PSS ink.

Figure 1 shows the morphological aspects of G-PEDOT:PSS ink. The microstructure shows that the G-PEDOT:PSS has a rough structure while the average size of the nanoparticle is about 60 nm (with 40,000x). The coexistence of Graphene and PEDOT:PSS proves the molecular binding.

Figure 2 shows the SEM images for the microstructure of G-PANI ink. G-PANI surface is smoother than the G-PEDOT:PSS ink, and hence it has more binding with the working electrode. As revealed from SEM images, some roughness is observed in the PANI layer. At 40,000x, the roughness is for nanoporous structure with around 1 µm diameter.

3.2 Electrochemical Response of G-PEDOT:PSS & G-PANI ink
3.2.1 Repeatability Test & Performance Evaluation of Proposed Inks

The potential for using Graphene conductive-based inks for DA detection is evaluated by cyclic voltammograms. To determine repeatability, we have used cyclic voltammetry to measure DA with Fe2+/Fe3+ redox couples using a bare screen-printed electrode. The electrochemical measurements have been carried out with three-electrode cells. To check the repeatability of the sensor, after each experiment, the sensor was washed with Phosphate Buffer Saline (PBS,1x) and left to dry for 30 minutes. After 30 minutes, the same experiment was conducted, and this procedure was repeated multiple times. Although, after the first
wash, the anodic peak current of the cyclic voltammogram has shifted slightly, washing the electrode with PBS (1x) multiple times do not have any effect on the sensor performance (Figure 3(a)).

![Cyclic Voltammetry](image)

Figure 3: Cyclic Voltammetry of 100 µM DA at 0.08 V/sec scan rate (a) repeatability test with bare screen printed electrode (b) Performance evaluation of G-PEDOT:PSS and G-PANI ink.

We have further investigated the performance of our proposed ink before and after multiple washes for DA detection. Our proposed inks significantly improved the detection of DA when compared to a bare screen-printed electrode. G-PANI ink has been proved to have better stability than G-PEDOT:PSS ink after the first washes. Before washing, the anodic peak current increased by 900 percent of 100 µM DA compared to the bare screen-printed electrode. After washing the electrodes with PBS (1x), some of the ink has been washed away, and it remained the same after multiple washes compared to the bare screen-printed electrode sensor. The anodic peak current increase is 102.9 percent after multiple washes.

From Figure 3(b), it is evident that G-PANI provides a higher redox peak than G-PEDOT:PSS and bare electrode. The anodic peak current increases by 25 times than the bare screen printed electrode before wash. After washes, the anodic peak current increases by 17 times. G-PANI ink-modified electrodes provide better stability after multiple washes than G-PEDOT:PSS ink.

### 3.2.2 Different Concentrations of Dopamine and LOD Detection

Response characteristics of DA with varying concentrations (50 µM- 800 µM) are determined by Cyclic Voltammetry. We have used two-fold serial dilutions method to prepare different concentrations of DA. The CV curves for DA at various concentrations are shown in Figure 4 using (a) a bare screen-printed electrode, (b) a screen-printed electrode with G-PEDOT:PSS ink and Figure 5 (a) screen-printed electrode with G-PANI ink after multiple washes. Additionally, the calibration curve for G-PEDOT:PSS ink ($R^2=0.94889$) and G-PANI ink ($R^2=0.9602$) are given. The limit of Detection calculated (assuming S/N=3) for G-PEDOT:PSS ink is 118 µM and for G-PANI ink is 101.374 µM by using the formula,

\[ \text{LOD} = \frac{3 \times S_b}{m}, \]

where $S_b$ is the standard deviation of the blank signal and $m$ is the slope of the calibration curve.

![Cyclic Voltammetry](image)

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![Cyclic Voltammetry](image)
Figure 4: Cyclic Voltammogram for varying different DA concentrations (50-800 µM) after multiple washes (a) bare screen printed electrode (b)G-PEDOT:PSS ink and (c) Calibration curve of G-PEDOT:PSS ink.

Figure 5: Cyclic voltammogram for varying different DA Concentrations (50-800 µM) after multiple washes (a) G-PANI ink (b) calibration curve of G-PANI ink.

3.2.3 Selective Detection of Dopamine with Ascorbic Acid

DA and AA resides together in the extracellular fluid of the central nervous system. It is a challenging electrochemical analysis technique to differentiate the components as many electrodes have identical oxidation potentials. Graphene based conductive inks show tremendous improvement in selectivity due to the remarkable promoting properties of graphene toward DA and AA. Sp² conjugated link in the carbon lattice offers high conductivity of graphene. Additionally, the molecular structures of DA and AA are distinct from one another. Because of the interaction between the phenyl structure of DA and the two-dimensional planar hexagonal carbon structure of graphene, electron transport takes place. AA has a weak interaction with Graphene and the effect of AA almost remains inactive in the G-
PEDOT:PSS and G-PSS ink. From the figure 6(a), it is visible that the anodic peak current of 100 µM DA is around 18.87 µA at 0.1465 V with G-PEDOT:PSS ink. When 250 µM Ascorbic Acid is added with 100 µM DA, the peak of anodic current shifts towards right at 0.203 V with a value of anodic peak current 14.58 µA. So, there has been a change of 38.57 percent change in voltage with the interference of Ascorbic Acid. After adding 500 µM Sodium dodecyl sulfate (SDS) with Ascorbic Acid and Dopamine, the anodic peak current is at 0.1463 V which shows the selective detection of Dopamine with G-PEDOT:PSS ink and SDS. Selective detection of Dopamine with G-PANI ink is shown at the figure 6(b). From the figure 6(b), it is evident that after adding AA with dopamine, there is a slight change in the CV curve. Our proposed inks do not show distinct peaks for DA and AA, respectively, and therefore, the inks do not offer that much selectivity. We will be working on modifying our inks so that the inks can offer better selectivity without any interference from AA.

4. CONCLUSION

In this research paper, we have developed Graphene conductive ink-based electrochemical sensor platform for sensitive, selective, low-cost, and rapid detection of DA. Graphene-Polyaniline (G-PANI) shows the best result in terms of sensitive and stable detection. G-PANI ink is more stable than G-PEDOT:PSS ink after multiple washes with PBS (1x) with a better LOD of 118 µM compared to G-PEDOT:PSS ink (LOD-101.374 µM).

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