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Graphene based biosensors for detection of neurotransmitters

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Introduction

Neurotransmitters are the brain chemicals that are used to convey information throughout the body through neurons. The human brain uses these chemicals to maintain the functional activities of central nervous, cardiovascular and hormonal systems. Neurotransmitters has significant role in regulating cognitive functions and it's the abnormal levels leads to neurological disorder illness in human body. The neurotransmitters are of two type as Inhibitory and excitatory. The excitatory neurotransmitters are essential to stimulate the brain, whereas inhibitory helps to calm down the brain and create balance throughout the body. Among the various neurotransmitters, the monoamines are histamine, adrenaline, dopamine, noradrenalin, serotonin and melatonin are of potentially important. In neurotransmission process dopamine acts as extrasynaptic messenger and considered as unique one as it possess both excitatory and inhibitory functions. Further the abnormalities of dopamine leads to Parkinson's disease, attention deficit hyperactivity disorder.

In addition use of illegal drugs namely heroin, cocaine and nicotine blocks the dopamine uptake and increase the risks of depression and drug addiction. Dopamines being electrochemically active species, several electrochemical techniques are employed to detect even low levels of dopamine. The major problem dealt with this electrochemical detection is that the presence of the interfering compounds such as uric acid and ascorbic acid. Uric acid is produced as a result of metabolism of purine whereas the ascorbic acid acts as reducing agent and helps in protection against biological oxidation process. Since ascorbic and uric acids have similar oxidation potential they usually overlap the dopamine oxidation peaks and hence make difficult to distinguish separately. Moreover the oxidation of these interfering compounds fouls the working electrode surface in electrochemical process and leads to poor sensor performance. Hence surface modification of electrode becomes essential for effective and sensitive detection of dopamine at low concentration with improved sensing range.

A two dimensional planar sheet of sp2 bonded carbon atoms arranged in hexagonal honeycomb configuration – Graphene, attracted several research communities owing to exceptional electronic and physical properties.[1] Graphene is ideally employed in several electrochemical applications due to its large surface area, higher electron mobility and unique heterogeneous electron transfer rate with lower cost in production. Several forms like thermally, chemically and electrochemically reduced graphene oxides with oxygen functional groups and defects are employed for electrochemical detection. The surface edge planes and defects possess rapid electron transfer compared to basal planes for electrochemical sensing applications. Further the presence of oxygen functional groups on the surface of graphene facilitate enhanced adsorption of analyte of interest and effectively catalyse them. Hence lot of attentions are focussed on graphene based materials for developing dopamine sensing devices.[2]

The sp2 hybridization, ballistic conduction and the presence of oxygen functional groups of graphene accelerate the electron rate transfer capability. The phenyl structure with π electrons effectively interact with the dopamine aromatic ring and significantly enhances the redox reactions with suppression of interfering ascorbic acid peak due to electrostatic repulsion between graphene oxide and dopamine. Further, the π-π interaction between aromatic structure of graphene and dopamine effectively enhances the faster electron rate and decline the oxidation of ascorbic acid. Chemical doping of Graphene with hetero atoms are of greater interest where the entire physio-chemical properties gets tuned up due to the dopant ion incorporation. Nitrogen doped graphene is of particular interest due to its comparable atomic size and presence of five valence electron where it can form strong bond with carbon atoms. Further doping with electron rich nitrogen atoms may lead to increase the free charge carrier range and contribute to enhanced electron transport property. The hydrogen bond formation between nitrogen doped graphene and amine/hydroxyl group of dopamine contribute to excellent electro catalytic activity and decrease the potential overlap due to interfering compounds.

The functionalization of graphene surface with metal and metal oxide nanostructures further improves the electron transfer rate and enhances the sensing characteristics. The covalent and non covalent modification of graphene surfaces with polymers have also been utilized for the superior sensing of dopamine.[3] Nanosized metal or metal oxides exhibit better physical, chemical and electronic property compared to bulk structures. In most cases nanoparticles are prepared in the reaction environment where stabilizers are present, thus contributing to charge, stability and solubility. Thus when the surface of graphene are modified with these nanoparticles they provide large surface area, increased mass transport rates, better control and show unusual transport properties where the modified electrodes show sluggish transport behaviour. Apart from metal and metal oxide nanostructures, graphene surface modified with polymers are of special interest owing to its excellent catalytic activity. The polymers include electro active, polyelectroactive, coordinating and biological polymers. The major advantages of polymer modified surface are facilitating the counter ion incorporation against the analyte of interest, interference avoiding by selective coating, electronic chattels as compared to metal / metal oxides and prevention of electrode fouling or poisoning by formation of protective surface .[4,5] The other class of nanomaterials includes the one dimensional structures like nano rods, wires and tubes decorated on the surface of graphene explored for dopamine sensors. Though the structures they look alike they have variations in their lengths and diameters.[6] These variations in length and diameter provide diverse improved properties for effective sensing of dopamine.

Conclusion

Thus to summarize, the sensitivity of the dopamine detection by using graphene can be accelerated by various process like surface modifications and functionalization with suitable materials. Surface area of the modified electrode expected to be an important parameter in providing superior sensing performance where more functional groups are exposed to the analyte of interest. The functionalization provides selective binding of analyte of interest and ion-exchange which repels the interfering effects on dopamine. Further, the graphene based dopamine detection lacks understanding the exact mechanism and long term stability which needs further examination to have better sensing of dopamine.

Acknowledgments

None.

Conflicts of interest

None.

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