CONTROLLED AGGREGATION OF GRAPHENE NANOSTRUCTURES USING NOVEL FUNCTIONALIZATION TECHNIQUES AND THEIR APPLICATION IN ELECTROCHEMICAL BIOSENSORS

A Thesis submitted in partial fulfillment for the Degree of

Doctor of Philosophy

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INDIAN INSTITUTE OF SPACE SCIENCE AND TECHNOLOGY THIRUVANANTHAPURAM JUNE 2018

Abstract

Over past two decades, there has been an intense focus to understand and extend the technological boundaries of carbon-based nanomaterials such as graphene, carbon nanotubes and fullerene. Among these, due to the excellent electrical conductivity, tuneable band gap, fast electron transfer, facile synthetic routes, graphene have captivated the attention of electrochemical community. Despite the excellent properties, the restacking property of graphene limits its application. Although there was a substantial methods of functionalization, where functionalized graphene have scrutinized, there is still room for exploration. We have synthesised graphene *via* chemical method, functionalized by plasma functionalization method, and hybridized with nanomaterials, studied the electrochemical properties and demonstrated its biosensor applications for the detection of various bio analytes. The studies conducted using various forms of graphene given in this Thesis is briefed below.

Nitrite is an important molecule, which has both biological and environmental significance. An electrochemical sensor, which operates *via* direct electron transfer (DET) mechanism is explored for the nitrite detection using graphene functionalized by ammonia radio frequency (RF) plasma. Here, hemoglobin immobilized on functionalized graphene was used as the bioreceptor. The detection limit of this sensor system was 1.3 nM. Selectivity was demonstrated using other endogenous species like ascorbic acid, uric acid and hydrogen peroxide.

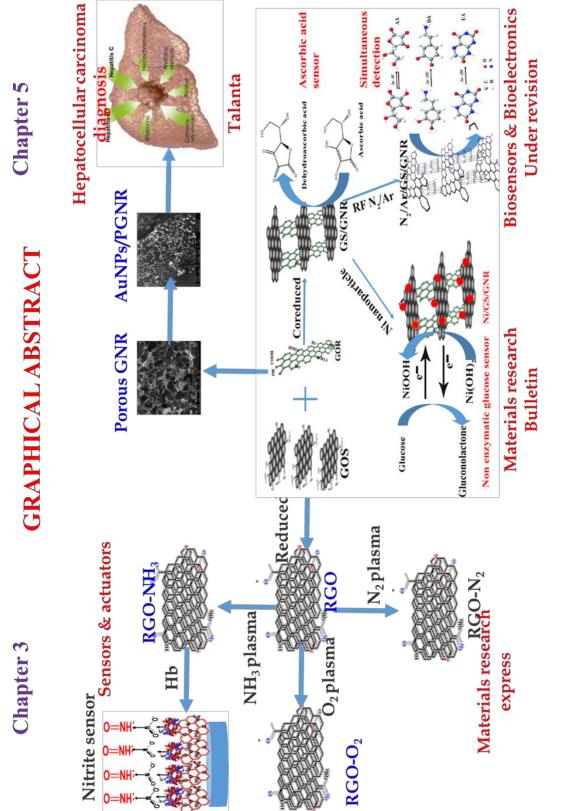
Hybridized graphene with enhanced surface area and excellent electrical conductivity was prepared by incorporating graphene nanoribbons (GNR) into graphene sheets (GS). A detailed microscopic, spectroscopic and surface area analysis confirms that the GNR was introduced into GS. A selective electrochemical sensor for the detection of ascorbic acid (AA) using GS/GNR was also accomplished with high sensitivity of 22 nA/ μ M cm² and detection limit of 230 nM.

The electrochemical performance of GS/GNR was enhanced by introducing nitrogen heteroatom *via* nitrogen/argon (N₂/Ar) RF plasma functionalization. N₂/Ar/GS/GNR has enhanced electrocatalytic activity and wide potential window

employed for simultaneous detection of ascorbic acid, dopamine and uric acid with well-resolved peak separation potential ($\Delta E_{AA-DA}= 220 \text{ mV}$, $\Delta E_{DA-UA}= 152 \text{ mV}$, $\Delta E_{AA-UA}= 372 \text{ mV}$). The detection limits of AA, DA and UA were estimated to be 5.3, 2.5 and 5.7 nM, respectively.

Nickel (Ni) nanoparticles with excellent electrocatalytic activity was incorporated into GS/GNR through chemical reduction method. A detailed characterization on crystallinity, morphology and spectroscopy confirms the incorporation of Ni into GS/GNR. Highly sensitive electrochemical sensor for the detection of glucose using Ni/GS/GNR was also accomplished at an applied potential of +0.5 V with a detection limit of 2.5 nM and sensitivity of 2.3 mA/mM cm².

Porous GNR, which increases rate of diffusion of ions, was synthesized by chemical etching of iron oxide nanoparticles. To enhance the electrochemical property and for providing an immobilization platform for biomolecules, porous GNR was electrochemically deposited by gold nanoparticles (AuNPs). Finally, a novel AuNPs/Porous GNR electrochemical immunosensor was fabricated to diagnose hepatocellular carcinoma with a wide range of linear response (0-60 ng/ml), detection limit (1 ng/mL), high sensitivity, good repeatability, and long-term stability.



Chapter 4

xi