Carbon Materials and their Composites for Device Applications

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Doctor of Philosophy

By

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Chapter 7

7.1 Summary and Conclusions

The current chapter highlights the conclusions of the thesis and suggested future research directions. The emphasis of this work has been on the synthesis of carbon nanomaterials, specifically graphene oxide (GO), reduced graphene oxide (rGO), graphene quantum dots (GQDs), and their nanocomposite with conductive polymer PBTTT, namely PBTTT/GO, PBTTT/GQDs for thin film transistor application, and finally biomass-derived activated carbon for electrochemical sensing applications. The major goal of our research is to investigate the floating film transfer method (FTM) for the development of low-cost, solution-processable, large-area polymeric thin film transistor fabrication. The literature on the fabrication of low-cost, stable, and high-performance polymeric thin-film transistors is still underdeveloped. In addition, for the electrochemical sensing application, because of their high electrical conductivity, precise microstructure, and outstanding stability, carbon-based materials have shown a lot of attention as electrode materials. Carbon compounds of this type can be designed to have high sensitivity and selectivity. Aside from graphene and CNT-like materials, it's also critical to investigate environmentally benign, effective, and cheap carbon compounds for a variety of applications. Because of high surface area, low toxicity, changeable pore size, good electrical conductivity, chemical stability, and presence of heteroatoms that give good functionality, biomass-derived activated carbon materials have been receiving serious interest in this direction. This thesis is well-organized around the synthesis of carbon nanomaterials and their nanocomposites for device application. The following is a chapter-by-chapter synopsis of the thesis:

Chapter 1 gives a brief introduction to carbon materials, synthesis, properties and their various technological application. This chapter offers a literature assessment to identify research needs as well as incentives for using carbon nanomaterial characteristics in device applications. In the context of polymeric thin film transistors, Conductive polymers (CPs) are a type of organic semiconductor with unique electrical and optical characteristics. It is surpassing amorphous silicon in the electronic sector due to its minimal cost, material processability, lightweight, customizable electrical conducting characteristics, and flexibility. Supercapacitors, light-emitting diodes, solar cells, field-effect transistors, sensors, biosensors, batteries, and corrosion inhibition are just some of the applications for conductive polymers and composites. Conducting polymers such as

polypyrrole, polyaniline, and polythiophene were used as active materials in these devices. Processability into a thin film on different substrates and measures of selecting materials with good electrical conductivity from the perspective of an organic polymer electronic device. The economic issue is equally crucial, but it can be overlooked due to the greater quality of the product line. Researchers are working on establishing a dependable technique for incorporating organic material in low-cost gadget manufacture. Another significant factor to consider when choosing a material is its electrical structure. Organic molecules are resistant to alteration in their assembly (ordering of π-conjugated polymer chain) due to molecular interactions. To increase the crystallinity of CPs, molecular interactions can be adjusted by providing templates or self-assembly. Mobility in large-area electronics applications can be boosted by aligning CPs' charge carriers. Carbon-based nanofillers have been frequently used to convey their high mechanical toughness, as well as outstanding thermal and electrical conductivity, to the macroscopic system in nanocomposites with polymer matrix. Examples include carbon black (CB), extended graphite (EG), carbon nanofiber (CNF), carbon nanotube (CNT), and graphene. The presence of mobile electrons is responsible for graphene and graphene's derivatives' extraordinary electrical conductivity. Because of its monolayer structure, graphene has a very low aspect ratio. Fillers with both incredibly low and high aspect ratios result in extremely low percolation thresholds, according to a recent survey. Conductive networks can be generated at very low filler concentrations when graphene or carbon nanotubes are coupled with a polymer matrix. Therefore, researchers are attempting to combine graphene into graphene-polymer nanocomposites for these reasons.

These goals were determined by a literature assessment and consideration of the laboratory's facilities, which are listed below:

- To produce 2-D carbon nanomaterials/carbon nanocomposites in a variety of ways and characterise them for device applications.
- The optimization of the lengthy thin film deposition techniques that are commonly used for the manufacture of polymer thin films as gas sensors, such as physical vapour deposition, chemical vapour deposition, spin coating, LB or LS technique, and so on.
- Low-cost fabrication of huge roll-to-roll flexible electrical gadgets.

- Surface modification, chemical dipping, doping, and other extra treatments to increase sensor performance are minimised.

In the context of electrochemical sensing applications, electrochemical sensors provide reliable analytical procedures that sidestep the constraints of quick, sensitive, and specific analyte determination. Electrochemical sensors transform information from analyte-electrode reactions into qualitative or quantitative outputs. Electrochemical sensors, unlike other detection methods such as chromatographic or spectroscopic, can be reconfigured to detect a vast diversity of analytes while remaining affordable.

They can also be integrated into durable, portable, miniatured devices, allowing for custom applications. For use in electrochemical sensors, fresh and novel materials are widely investigated. The materials used to support the surface or electrodes are usually benign, containing no electroactive species, and conductive over a wide potential range. Carbon is widely used in sensor applications due to its relatively neutral electrochemistry and electrocatalytic activity for a range of redox reactions, as well as its minimal prices. Biomass-derived porous carbon composites have been touted as attractive alternatives for building environmentally friendly energy storage devices and ultrahigh-performance sensors in recent decades. Activated carbons (ACs) can be made from biowaste in a simple, environmentally preferable, and budget manner. Due to their unique properties, such as porous structure, tunable pore size, low toxicity, chemical inertness, high conductivity, and the existence of oxygen surface functional groups like heteroatoms, ACs prepared from numerous biowaste have been widely used in a variety of applications. This chapter deals with methods for synthesising distinct carbon structures from various bio-precursors. The influence of activation on the electrochemical sensing capability of biomass-derived carbon-based electrodes is discussed in this paper. The activation operations are carried out to increase the surface characteristics and improve electrocatalytic sensing. However, activation may not ensure improved sensing performance, as only a few bio-precursors created hierarchical micro/meso/macro pores based on lignocellulosic content without activation, which were sufficient for superior sensing performance. Edge flaws and turbostratic character, as well as the existence of pores, all play a key role in improving electrochemical sensitivity. Due to micro/mesopores and the synergetic influence of doped atoms onto the carbon matrix, hierarchically porous and doped carbon materials also exhibit outstanding electrochemical performance. For newer electrodes, biomass-derived

porous carbon can operate as a distinctive host material for inserting metal ion inorganic complexes, noble and catalytically active metals, which can improve sensor performance.

Chapter 2 deals with the main fabrication tools used for the production as well as the characterization of an OTFT gas sensor and electrochemical drug sensor are briefly described. It includes equipment such as a vacuum coating unit, an oxidation furnace, an electric oven, a device characterization and gas sensing setup, grazing incident X-ray diffraction (XRD), scanning electron microscopy (SEM), an Atomic Force Microscope (AFM), kelvin probe force microscopy(KPFM), a High-Resolution Transmission Electron Microscope (HR-TEM), Fourier Transform Infrared Spectroscopy (FT-IR), UV-visible Spectroscopy, and Raman spectroscopy. Autolab was used to conduct the electrochemical experiments (CV, DPV, and EIS) (PGSTAT, 302, the Netherlands). For electrochemical investigations, a three-electrode assembly was used, consisting of a glassy carbon electrode (working electrode, diameter = 3 mm), a Pt-foil electrode (counter electrode), and Ag/AgCl (reference electrode). Palm Sens, the Netherlands, provided the screen-printed carbon electrode (SPCE) (Model number IS-1) with a reference electrode (area = 1 mm^2), a working electrode (diameter = 2 mm), and a counter electrode (area = 3 mm^2), which was further modified by the generated 2D carbon. The functioning principle and visual presentation of the various instruments and equipment were discussed. The detailed manufacturing process flow for OTFT devices was also described in this chapter.

Chapter 3 demonstrated with the ability to build a high-performance electronic device at a much lower cost and time than that required to make conventional devices is critical to a polymer's or nanocomposite's practical application. The Floating Film Transfer Method was used to help in the self-assembly of a highly-oriented crystalline polymer nanocomposite thin film of poly[2,5-bis(3-tetradecylthiophen-2-yl)thieno[3,2-b]thiophene] [PBTTT] and graphene oxide (GO) with a significant surface area at the air-liquid interface (FTM). The polymer nanocomposite thin film was studied using a variety of techniques, including scanning electron microscopy (SEM), high resolution-transmission electron microscopy (HR-TEM), selected area electron diffraction (SAED), atomic force microscopy (AFM), grazing incident X-ray diffraction (GIXD),

electronic absorption, Fourier transformed-infrared (FT-IR) spectroscopy, and atomic force microscopy (AFM), grazing incident X-ray diffraction (GIXD), electronic absorption, Fourier transformed-infrared (FT-IR) spectroscopy, and cyclic voltammetry (CV). The findings are also compared to pristine polymer thin film results. Furthermore, in ambient settings, the organic thin film transistors (OTFTs) produced using the polymer nanocomposite demonstrate superior device performance, with 0.112 cm^2 V^{-1} s^{-1} field effect mobility and 10^3 on/off ratio. Our research focuses on a technique that enables the rapid creation of good-quality self-assembled nanocomposite thin films for improved device efficiency.

Chapter 4 illustrated the ultrasonication technique in making solution-processable PBTTT/rGO nanocomposites in chloroform. Long-range ordering and crystallinity have been significantly enhanced in polymer chains with 2-D rGO nanosheets. In addition, an FTM technique based on a liquid base with a high surface free energy was developed to create self-assembled, highly oriented, anisotropic thin films of PBTTT/rGO nanocomposites. Numerous morphological analysis techniques, including transmission electron microscopy, atomic force microscopy, selected area electron diffraction, and others, show the formation of edge-on oriented, uniformly dispersed nanosheets in a polymer matrix as well as the growth of interconnected crystalline regions. This is in contrast to a matrix made entirely of polymers. The interaction between the polymer and the nanosheets, as well as the ordering of the polymer chains, can be seen in the UV/vis spectra of pure PBTTT and PBTTT/rGO nanocomposites. Additionally, CV demonstrates how the electrical characteristics and HOMO level change after the composite film is formed. Finally, a polymer nanocomposite thin film is used to create organic field effect transistors (OFET). With average mobility of 0.26 $cm^2V^{-1}s^{-1}$ at a drain voltage of -40 V, OFET made of PBTTT/rGO film has a higher device efficiency in atmospheric conditions. The mobility of PBTTT/rGO nanocomposite OFET is approximately 22 times greater than that of pristine polymer (=0.012 cm2 /V.s) and has more than four times greater on/off ratio (~1.3 x103). Our study reveals a technique to rapidly fabricate high-quality nanocomposite thin films for enhancing device performance.

Chapter 5 demonstrated the creation of graphene quantum dots (GQDs), which were subsequently used to create solution-processable PBTT/GQDs nanocomposites in chloroform. Additionally, a straightforward method for fabricating highly orientated,

lined-up films of PBTTT/GQDs nanocomposite is demonstrated. This method is executed at the air/liquid interface and is referred to as the floating film transfer method (FTM). Studies on surface morphology, like TEM, display the distribution of GQDs in the polymer medium. The well edge-on oriented thin film is confirmed by XRD and HR-TEM. The molecular interaction between polymer and GQDs is confirmed by UV-vis and FTIR spectroscopy. The cyclic voltammetry study illustrates how the inclusion of GQDs as filler changed the polymer's HOMO level, proving that the material's electronic characteristic has changed. Finally, top-contact bottom gate structures with gold metal electrodes are designed for device construction. According to research, the average field effect mobility of PBTTT/GQDs film is 0.16 cm^2/V.s, which is nearly 16 times greater than that of pristine polymer and has an on/off ratio of $0.56x10^3$(nearly 2.8 times that of pristine), under ambient settings.

Chapter 6 suggested that meso/microporous activated carbon be created as a long-lasting, environmentally benign, and simple-to-use material for electrode modification and further usage for the electrochemical sensing of arsenic-based medication ROX by DPV. XRD, Raman, and FTIR spectroscopies, as well as TEM and SEM, were used to analyse the 2D carbon as it had been formed. Using N_2 adsorption-desorption isotherms and BET measurements with a specific surface area of 194 m^2g^{-1}, the meso/microporous nature of AC was confirmed. When used to modify electrodes, commercially available graphite powder validated the performance of the as-synthesized 2D carbon. By comparing the EAS value of 2D-AC with that of Gr-modified GCE and bare GCE, which are 0.075, 0.065, and 0.052 cm^2, respectively, the superiority of 2D-AC was demonstrated. Based on an enzyme-free sensor, 2D carbon demonstrated outstanding electrocatalytic performance for the detection of the harmful substance roxarsone. The ROX sensor is created, developed, and performs well at - 0.66 V (versus Ag/AgCl) under ideal circumstances, possessing trustworthy sensitivity and LOD. Results indicate that affordably produced 2D carbon has the potential to be employed as an electrochemical platform for the catalytic ability of hazardous arsenic-based antibiotic ROX in real samples with a high recovery rate. The as-synthesized 2D-AC demonstrates that it is a promising electrode material and could be captured quickly. For selectivity, storage stability, and repeatability toward ROX, the designed sensor is validated. These results suggest it is a potential technique for electrochemical ROX sensing for chemical detection based on arsenic.

7.2 Future Work Plan

The future scope of the research is derived from the current work about the motivated aforesaid findings and the measurements made during the experiments. It offers several options for conducting research, some of which are included here.

(i) The thin film transistor which is fabricated using PBTTT/rGO and PBTTT/GQDs nanocomposite is further used in ammonia (NH_3) gas sensing and has shown good results.

(ii) Flexible sensors can be created using organic semiconductors that can be processed in a solution. Additionally, it is possible to investigate how mechanical stress affects OTFTs constructed on flexible substrates.

(iii) Synthesis of quantum dots of various 2-D materials can be utilised in gas sensing applications.

(iv) Synthesis of biomass-derived carbon having high surface area, less toxicity, adjustable pore size, good electrical conductivity, chemical stability, and the presence of heteroatoms that provide good functionality which is needed for the desired application.