A Study of Graphene based 2D heterostructures for high performance Supercapacitors

A Thesis Submitted in Partial Fulfillment of the Requirements for the Degree of

Doctor of Philosophy

Nithin Joseph Panicker

Registration No: TZ189867 of 2018

Roll No. ELP17102

DEPARTMENT OF ELECTRONICS AND COMMUNICATION ENGINEERING

SCHOOL OF ENGINEERING

TEZPUR UNIVERSITY

TEZPUR– 784 028, ASSAM, INDIA

December, 2022

Chapter 6

Conclusions and Future Scopes

Contents

6.1. Conclusions

The primary obstacle in the development of supercapacitors is their low energy density, relatively lower specific capacitance, and the usage of aqueous electrolyte. In this work, we had developed novel graphene based 2D/2D heterostructures and their nanocomposites with enhanced electrochemical performances for high performance super capacitor applications.

Initially, an introduction to supercapacitors, including its history, different types of supercapacitors, performance evaluation parameters, etc., is presented. A detailed literature survey on different graphene based 2D/2D heterostructures and their nanocomposites with metal sulfides and conducting polymers was discussed. In addition, different electrode materials and their performance characteristics are highlighted along with their shortcomings.

This research work aims to make significant contributions to the synthesis of novel electrode materials and the fabrication of high performance supercapacitors. Initially, a novel synthesis method of highly oxidized graphene (HOG) by using HNO_3 and $KMnO_4$ as oxidizing agents was developed. This method was found to be better than the existing Hummers method and Marcano's method.

A green method for the reduction of graphene oxide using phytochemicals extracted from Pomelo Grandis and Tamarindus indica was developed. FTIR analysis showed significant reduction/elimination of the peaks that corresponds to the oxygen containing groups. XRD and Raman analysis confirmed the successful reduction of GO after treating with fruit extracts. The morphological analysis by SEM and TEM images further confirmed the formation of graphene nanosheets. The conductivity of both Pomelo-rGO (P-rGO) and Tamarind-rGO (T-rGO) were found to be 10^4-folds higher than that of GO. This method was found to be green and cheap for mass production of reduced graphene oxide. It also avoided using harmful and toxic reducing agents and the byproducts were mainly organic compounds and water.

In this work, the synthesis of a novel band-gap tuned highly stable hexagonal-boron nitride/reduced graphene oxide superlattice wrapped cadmium sulfide/Polypyrrole nanocomposite as an efficient supercapacitor electrode material was reported. It was synthesized via hydrothermal method combined with chemical oxidative polymerisation mechanism. The liquid exfoliated h-BN and graphene layers are restacked randomly by properly sandwiching alternate layers to form band gap tuned h-BN/rGO hetero-structure contributing as a conducting framework due to formation of Van der Waals stacked superlattice. The restacking of rGO layers in between h-BN sheets lowers the offset Fermi level. As a result, there is a lowering of band-gap in h-BN/rGO superlattice promoting fast transfer of electrons in the nanocomposite through formation of conducting framework.

Further, the introduction of CdS nanoparticles (NPs) while restacking of h-BN and rGO nanosheets, entraps the CdS NPs in between the sheets forming a core-shell like structure. The h-BN/rGO-CdS core-shell structure inhibits the swelling and shrinking of CdS which improved the electrochemical performance and stability of the supercapacitor electrode. The similar band-gaps of h-BN/rGO (2.5eV) and CdS (2.40eV) enhances effective inter-charge transfer mechanism. The highly conducting PPy nanowires acts as a backbone for the fast conduction of ions and the porous structure exhibiting superior specific capacitance of 1435F/g at of 1A/g. The asymmetric supercapacitor (ASC) fabricated using h-BN/rGO/CdS@PPy//AC presented a specific capacitance of 102F/g at 1A/g and maximum energy density of 32Wh/kg at a power density of 750W/kg. Furthermore, the device showed a capacitance retention of 88.50% after 5000 cycles assures it as best choice for supercapacitors.

This thesis also presents a novel hierarchical porous N, S doped reduced graphene oxide- $NiCo_2S_4$ hybrid nanocomposite was synthesized by in-situ growth of $NiCo_2S_4$ over porous rGO framework by a facile hydrothermal procedure. The materials are optimized by determining the proper ratio of metal ions to graphene in order to obtain optimal supercapacitive performance. The optimum use of materials showed improved nucleation and confined growth of $NiCo_2S_4$ nanoneedles over rGO by taking the advantages of high specific surface area and porosity of rGO. The N,S dual doping further enhanced the electrochemical activity by introducing defects in the surface morphology and altering the uniformity of graphene thereby preventing aggregation. The prepared GNCS3 electrode showed exceptional specific capacitance (1640F/g at current density of 1A/g). The enhanced electrochemical activity is due to the synergetic impact of $NiCo_2S_4$ and rGO, wherein rGO served as an excellent conductor and ideal framework. The all-solid-state GNCS3//AC ASC fabricated showed outstanding electrochemical properties with a specific capacitance of 135F/g at 1A/g, excellent capacitance retention of 92.5% after 5000 cycles and highest energy density of 27Wh/kg at an power density of 600W/kg. The facile synthesis and excellent capacitive behaviour of $NiCo_2S_4$/rGO makes it an ideal electrode material for supercapacitor applications.

In this thesis, porous carbon self-repairing g-C_3N_4 (pCCN) nanosheets were synthesised by a solvothermal process followed by thermal treatment in air and acid treatment. A facile hydrothermal process is employed for the confined growth of $NiCo_2S_4$ nanoneedles on porous carbon self-repairing g-C_3N_4/rGO heterostructure as hybrid material for supercapacitor electrodes. The improved electronic conductivity and activity of carbon self-repairing g-C_3N_4 (CCN) than g-C_3N_4 because of the creation of extended delocalized π-electron by the

substitutional or interstitial C atoms in the structure and because of acid treatment, the larger planes of CCN are broken down into smaller segments, increasing the edge nitrogen and oxygen functional groups. The introduction of porous CCN led to the strong electrostatic interaction with GO and CCN which aided in the suppression of agglomeration of graphene sheets. The as-synthesised pCRNCS electrode demonstrated exceptional specific capacitance (1938F/g at current density of 2A/g). The excellent electrochemical activity is because of the combined effect of large surface area rGO and extended highly reactive region and defects in pCCN which facilitated the nucleation and confined growth of $NiCo_2S_4$ nanoneedles in the framework. The constructed pCRNCS//AC ASC exhibited remarkable electrochemical properties, including a specific capacitance of 211F/g at 1A/g, an exceptional capacitance retention of 93.6% after 6000 cycles, and the maximum energy density of 66Wh/kg at a power density of 751W/kg. The exceptional capacitive behaviour of porous carbon self-repairing g-C_3N_4/rGO@$NiCo_2S_4$ makes it an ideal choice for supercapacitors.

6.2. Future Scope

Despite the substantial progress made during the course of this thesis, there are still obstacles to overcome in order to raise the specific capacitance and true specific energy density of supercapacitors without compromising their power density and safety.

6.2.1. Potential window

The supercapacitors' energy density is linearly related to the square of potential window. Hence, a small increase in potential window can yield a substantial increase in the energy density of the device. The potential window achieved in this research is limited due to the use of aqueous electrolyte and PVA/KOH gel electrolyte. The potential window of aqueous electrolytes is restricted due to the electrolysis of water. Organic electrolyte with high potential window could be tested with the developed nanocomposite for high energy density supercapacitors.

6.2.2. Non-toxic, highly flexible, non-liquid electrolyte

The electrolyte used in this research are water based with water soluble polymer or alkali which are corrosive in nature. Also, water-based electrolytes suffer from evaporation problem that will affect the lifetime of the device. This problem also limits the choice of device packaging and field of application. These issues can be resolved by introducing non-hazardous materials, polymers, and solvents with low evaporation rates to the electrolyte. Additionally, the final device needs a suitable packaging method to enclose it in a fine polymer film that can be integrated into wearable electronic systems.

6.2.3. Flexibility

The supercapacitors developed in this research work are non-flexible in nature. With the rapid development of portable electronic gadgets and the concept of wearable electronics, flexible energy storage systems have gained popularity amongst researchers. It is of critical importance to design energy storage systems that are both flexible and compact, but also possesses excellent electrochemical characteristics. Further study is needed to develop flexible devices which requires the development of flexible current collectors, electrode materials, binding agent, etc.

6.2.4. Scalability and Cost of production

It is necessary to develop supercapacitor banks and choose the best supercapacitor cells for future scaling up. Performance in terms of power and energy density should be taken into account, as well as cost for large-scale commercial production. Additional research is required to evaluate the business case, economic viability, and environmental sustainability of the suggested supercapacitors for use in electric vehicles. Further study is required to create recycling methods and routes for all carbon-based components of the proposed supercapacitors. The synthesized materials can also be used in water splitting applications and hydrogen fuel cell applications.