Abstract

The over exhaustion of non renewable energy sources and the ever increasing demand for energy led to the development of renewable energy conversion and storage devices. In this context, supercapacitors gained much momentum as an energy storage device with better specific capacitance, fast charge-discharge, high power density, cycling stability, etc. Supercapacitors are widely employed as temporary energy storage to counter the voltage variations in power grids, in tandem with batteries in electric vehicles, for voltage stabilization in solar, wind energy etc. The main challenge in the development of supercapacitors is their low energy density, comparatively lesser specific capacitance and use of aqueous electrolyte. Therefore, novel materials and structures need to be explored for the design and development of supercapacitors, that are all-solid-state and potentially with higher energy density and specific capacitance. In this direction, graphene based heterostructures and their nanocomposites seems to be a good electrode material for the development of high performance supercapacitors. There are not much research done on graphene based heterostructures for supercapacitor applications, hence there is ample scope to improve the properties of the electrode material in terms of material morphology and electrochemical properties.

This thesis 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.

Then, 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 thesis, a band-gap tuned highly stable h-BN/rGO wrapped CdS/PPy is presented as a supercapacitor electrode material to obtain excellent specific capacitance, high power density and long cycling stability. 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 h-BN/rGO-CdS core-shell structure prevents the swelling and shrinking of CdS which improved the electrochemical performance and stability of the supercapacitor electrode. 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 a current density of 1A/g. The asymmetric supercapacitor (ASC) fabricated using h-BN/rGO/CdS@PPy//AC showed 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 a promising material for supercapacitor application.

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 process. 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 exhibited high specific capacitance (1640F/g at current density of 1A/g). The improved 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 excellent 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 prepared by a solvothermal process coupled with post 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 due to the formation 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 exhibited high specific capacitance (1938F/g at current density of 2A/g). The excellent electrochemical activity is due to the synergetic effect of high 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 excellent capacitive behaviour of porous carbon self-repairing g-C_3N_4/rGO@$NiCo_2S_4$ makes it an ideal electrode material for supercapacitor applications.

Finally, it is concluded that the fabricated supercapacitor results are very promising for use in different commercial and defence applications. Also, future scope for the improvement of the work in the related area has been presented, based on the constraints and limitations of the present study.