Preface

The sustainable supply of energy, in various forms, is a critical issue the modern world. Both the energy generation, from renewable/non-renewable resources, and the energy storage are critically important aspects of energy science. A rapid raise in the world’s population and the technological developments are the mains reasons for a high rate of world’s total energy consumption. This led to the fast depletion of energy resources and enhancement environmental pollutions. To overcome these problems there is an urgent need to develop a greener approaches for the conversion/generation of energy and its storage. Among various forms of energy, the electrical energy is one of the most indispensable energy because of its high consumption in various applications like lighting, warming and cooling, from cooking to entertainment, transportation and communication, as a primary source. It can be generated from many processes like fuel-burning power, nuclear power which are hazardous and environmentally not too safe but the production from solar power, hydropower, wind power, tide power and biopower systems, which are renewable, not hazardous and environmentally safe but are less efficient in the energy conversion. Hence, it is necessary to develop the technology for clean and sustainable production of energy from the renewable resources, also the new technologies to develop high energy storage systems. Worldwide there has been a focused research activities in these directions. The main focus is on the conversion of solar energy to electricity using photovoltaic devices. However, the availability of this energy on the earth’s surface is only intermittent but the energy consumption is a continuous process.

As a result, the energy storage becomes critically important issue and it also must be developed in parallel to the energy conversion process. The new techniques are needed to enable efficient, versatile and user friendly energy storage devices.
Therefore, the scenario demands new energy storage devices that can support the sustainable development of the global economy and the society. The only way to address these problems is new design and advanced development of energy storage systems using high-performance materials to store the energy generated that are low cost, easily implementable and environmentally friendly.

An electrochemical energy storage device converts chemical energy to electrical energy. In which the energy storage/release is realised by electron and ion charge/discharge between electrodes and electrolytic solution. There are mainly two kinds of energy storage devices, one is electrochemical batteries and another is supercapacitors, the latter is also known as electrochemical capacitor. Both store electricity in electrochemical processes. A simple electrochemical energy storage device is usually composed of an anode, a cathode, a separator soaked in an electrolytic solution. Li ion batteries are the most important and widely used rechargeable battery with high operating voltage, low self discharge, long cycling life, low toxicity and high reliability. These two types of energy storage devices as complimentary to each other, for example, the electrochemical batteries are characterized by high energy density, slow power and low life cycle whereas the supercapacitor is by high power density, high power delivery and long life cycle. The supercapacitors, are also known as ultracapacitors, is an electrochemical energy storage device with much larger capacity than conventional electrolytic capacitors (it is almost one million times), and its charging/discharging rate capability is much higher than primary/secondary batteries. Supercapacitors are environmentally friendly, highly safe and can be operated in a wide temperature range with a near-infinite long cycling life.
The charge storage mechanisms in these devices further divides them into two types. One is electric double layer capacitor which is quite similar to an electrolytic capacitor, in which the separation of charges at the interface between a solid electrode and electrolyte occurs. Another is a pseudocapacitor, here the charge storage is by fast faradaic process involving electrochemical redox reactions between the active surface atoms of electrode and electrolyte. However, recently it has been reported that the hybrid supercapacitors are combined with both of these properties.

The performance of these energy storage devices is completely dependent on the different types of electrode materials, electrolytes and the reversible electrochemical reactions between these two phases. It is necessary to think in this direction which evolves the development of new materials, new device structures and innovative hybrid interfaces on the electrode surfaces. In the recent time, a lot of work in these directions has been initiated by researchers but still to meet the high requirement, efficiency, stability and environmental friendly parameters further work is very essential to involves people from different disciplines like physics, chemistry, biology and engineering.

Nanomaterials are the potential candidates for the energy storage device applications because of their excellent physical and chemical properties. These are characterised by extremely small particle sizes that is just few nanometers in diameter with different dimensions (zero, one, two-dimensions). In general, they possess two important properties, one is size tuneable optoelectronic properties (due to quantum confinement effect) and second is the high density of surface dangling bonds. Nanomaterials aggregated to form spherical, tubular and irregular shape which gives high specific surface area in the small prescribed volume. The presence of large grain boundaries in these materials serves as a fast diffusion path for charges or active
species and increases the diffusion rate in an electrode-electrolyte assembly. Many nanostructured materials and their composites have been proposed as potential electrode materials on the basis of their unique appearance and surface morphology such as microporous scaffolds, nanotubes, nanofibers, nanohorn and hybrid nanostructures with high specific surface area. Also the carbon based materials are of great interest due to their abundance and tuneable pore structure by using the carbides and the chlorination at different temperatures. The optimised pore structure in these carbon based materials enhances the high specific surface area and the specific capacitance in supercapacitors. Also, the development of carbon materials with narrow pore size by using zeolite as a template increases the surface area which helps in diffusion of ions in a carbon based electrode. The conducting polymers and their composites with other suitable materials are also used as alternative electrode materials. The critically important parameters of electrode materials for supercapacitors applications are electrical conductivity, stability, internal surface area, pore size and the density of surface active atoms. On the other hand the significant parameters of electrolyte are stability, electrical conductivity, dielectric constant, cost and environmental friendliness etc.

Recently it has been observed that the surface modification of electrode materials by biomolecules/organic molecules enhances the performance of supercapacitors due to faradaic process. In these frameworks, organic molecules/biomolecules are connected through sulphur molecule on the surface of metal electrodes to form three dimensional networks on the surface of an electrode. The metal-organic frameworks and biomolecules-metal junctions are showing a significant enhancement in the value of specific capacitance. Hence, it is highly desirable to develop a new class of materials, their composites and heterointerfaces.
(by combining organic and biomolecules) as electrode materials for supercapacitors that can increase the specific capacitance and the energy density of these devices to match that of electrochemical batteries.

The aim of present thesis is to design and develop highly structured electrodes based on nanostructured materials that low cost and easy to process with a large physical size. In the first phase of the work, a choice of nanomaterials is made based on their good electrical conductivity, adherence and low cost to deposit on, highly porous and flexible such as polymers foams and cellulose materials. This work was further extended to thin film deposition of nanomaterials on the glass substrate based on pyrolysis technique. These materials are well characterized by known techniques to understand the materials parameters. Supercapacitor devices of various electrode materials and electrolytic solution are studied in detail on two electrode configuration by cyclic voltammetry measurements. A further work on surface grafting of linear organic molecules with sulphur end moiety is carried out to study their effect on devices. All the aspects are discussed in various chapters of the present thesis. Finally, the last chapter is devoted for summary and conclusion of the entire work and it also gives the scope for the future work. The present thesis has been planned in the following way:

**Chapter One:** This chapter begins with a brief introduction on the energy, energy storage devices, the storage mechanisms and different types of materials that are adopted to constitute the supercapacitors. The basic working principle of supercapacitors is also discussed. This serves as a good understanding of basic properties of energy storage devices. For this reason, an overview of the role of nanostructured materials, synthesis techniques, physical and chemical properties are
briefly explained. Different electrode configurations to understand the electrochemical property are briefly elaborated.

**Chapter Two:** It gives the experimental methods and characterisation techniques involved in the synthesis and characterisations of nanoparticles which are used to develop the composite electrode materials for materials for supercapacitors. In this chapter a brief discussion of preparation of nanoparticles by various methods are given.

A brief description and the working principles of various instruments that used in the present work will be discussed. These techniques include the X-ray powder diffraction (XRD), scanning electron microscopy (SEM), atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS) etc. The conductivity measurements (I-V characteristics) and the cyclic voltammetry (CV), charge/discharge curves for the calculation of specific capacitance are mentioned. Finally, a concise discussion on home-made contact angle measurement setup to check the hydrophilicity/hydrophobicity will be given.

**Chapter Three:** It describes the detailed studies on silver nanoparticles. A brief introduction is given on the past literature and related synthesis techniques of this material. Further the deposition of silver nanoparticles on highly porous structures like cellulose paper and polyurethane foam and the use of these films in constitution of supercapacitors are explained. Finally, the results and discussion of these electrode materials and their devices is given in terms of various properties, such as electrical conductivity, contact angle, SEM and XRD etc. followed by the characterization of their devices with respect to different electrolytes by cyclic voltammetry. The numerical values of specific capacitance and other parameters will be discussed.
Chapter Four: This chapter is devoted for copper sulphide nanoparticles. A brief introduction is given on the past literature and related problems of synthesis. Further the experimental techniques in which mainly the deposition of copper sulphide nanoparticles on highly porous cellulose paper to make highly conductive electrode for the application of supercapacitors is mentioned. Finally in the results and discussion the results and conclusions are drawn on these materials based on various characterizations. The cyclic voltammetry measurements will be discussed by constituting supercapacitors of these electrode materials using different electrolytes. Estimation of various devices parameters and their significance with respect to earlier work based on different potential materials will be discussed.

Chapter Five: This chapter is devoted to describe the detailed studies carried out on the antimony doped tin oxide deposited on glass and its surface modification by organic molecules are used to constitute the supercapacitors and the development of a cadmium oxide deposited on glass substrates as an electrode material for supercapacitors. In the beginning of each section, a brief introduction is given on the past literature of these materials. Finally, the results and discussions on various characterisation techniques (SEM, AFM, XRD and XPS) and the specific capacitance calculations from the CV curves and the stability test of these electrode materials will be discussed.

Chapter Six: This chapter is devoted to describe the detailed studies carried out on the development of graphene coated polyurethane foam as an electrode material for supercapacitors. In the beginning of each section, a brief introduction is given on the past literature of these materials. Finally, the results and discussions on various characterisation techniques (SEM, AFM, XRD and XPS) and the specific
capacitance calculations from the CV curves and the stability test of these electrode materials will be discussed.

Chapter Seven: This chapter is on the summary and the conclusions of the entire work of the present thesis. The present methods and techniques of making highly porous, conducting, hydrophobic, flexible, cost effective and lightweight electrodes and their devices will be summarised. At the end of this chapter, the further scope of the present work is given.