ABSTRACT

Due to global depletion of fossil fuels and simultaneous increase of environmental pollution there is a great demand for sustainable and renewable energy sources. In this context, supercapacitors or ultracapacitors have attracted as the promising alternative energy sources due to their high specific power density, long cycle life, fast charge/ discharge processes (within seconds) and low maintenance cost. Supercapacitors currently bridge the power gap between batteries and traditional solid state and electrolytic capacitors, delivering higher power bursts than batteries and storing more energy than capacitors. Owing to these unique properties supercapacitors are widely used in various energy storage fields such as energy back-up systems, consumer portable devices, electrical/ hybrid electric vehicles and other devices.

Based on the mechanism supercapacitors are classified into two categories: electrochemical double-layer capacitors (EDLCs) and pseudocapacitors. Generally, EDLCs based on carbon materials provide high cycling stability, but, they show lower specific capacitance and energy densities because charge is stored only on the surface area of an active EDLC electrode. Whereas, pseudocapacitors show high specific capacitance and energy densities due to charge store occurs by rapid redox reactions between the surface and the bulk of the electrodes. Hence, pseudocapacitors have been considered as the most attractive materials for energy storage applications. Among the reported pseudocapacitor materials, conducting polymer have drawn much attention due to their high conductivity, low cost, outstanding electrical and optical properties, flexibility. A.J. Heeger, A.G. MacDiarmid and H. Shirakawa were jointly rewarded with the Nobel Prize in Chemistry in 2000 for the discovery and development of conducting polymers. Among all conducting polymers, polyaniline (PANI) is one of the most significant conducting polymers, because of its relatively facile processability, electrical conductivity, environmental stability, high specific capacitance, redox activity and unusual doping-dedoping chemistry. However, the poor electrochemical stability of PANI due to the shrinkage of polymeric chains during redox cycling limits its applications in supercapacitors. Currently, many researchers are focused on supercapacitors to improve the energy density while maintaining high power density, fast charge/discharge and cycling stability. To achieve these objectives, there is a great need to synthesize various nanocomposites of PANI with carbon nanotubes, mesoporous carbon, graphene, transition metal oxides, and mixed metal oxides like spinel oxides. The

resultant nanocomposites show high cycling stability and specific capacitance due to synergistic effect of individual components.

Furthermore, it is reported that with increasing the pH typically at pH $\geq$4, the emeraldine salt form (ES) of PANI gets deprotonated and converts to the electrically non-conducting emeraldine base form (EB). This, ES-EB transition greatly limits the use of PANI in biomedical applications operating at the physiological pH=7.4. Therefore, the dopants which are biocompatible and can maintain electroactivity of PANI at higher pH values have gained much attention.

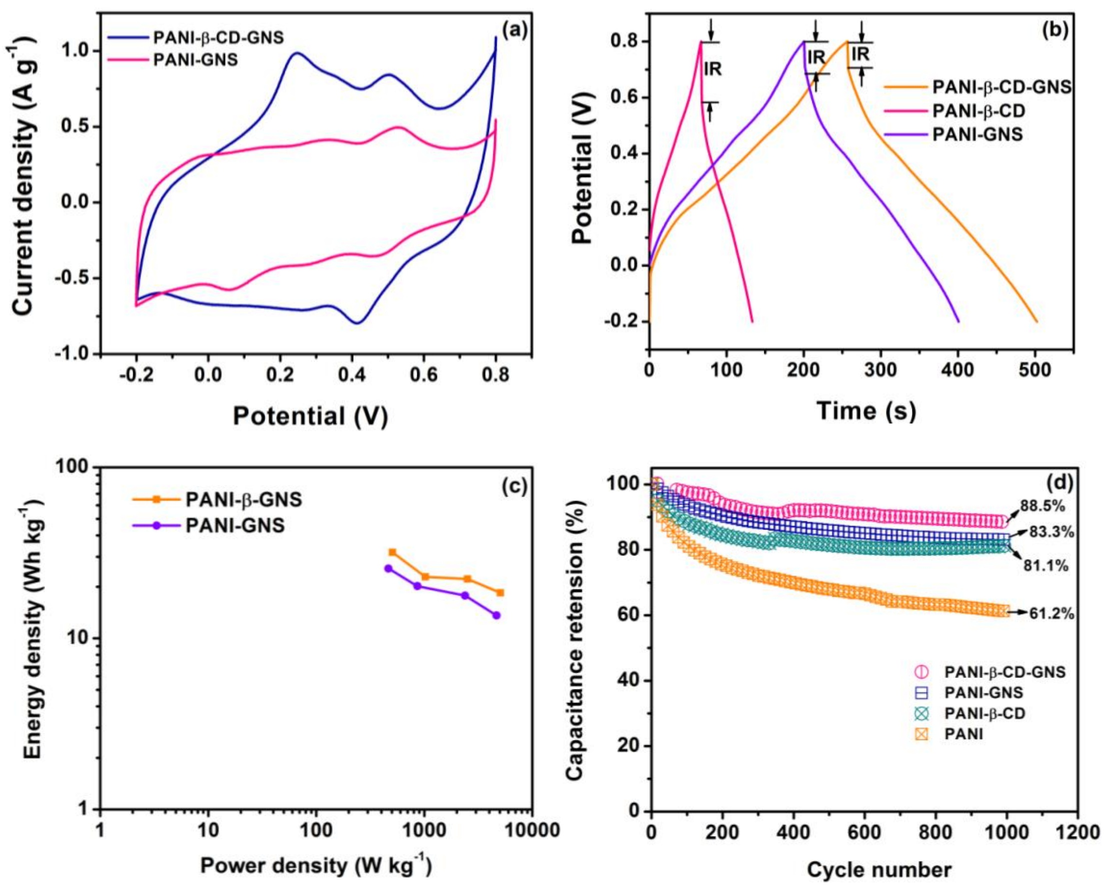
In this thesis, we are reporting PANI nanocomposites with graphene, spinel copper chromite ($CuCr_2O_4$) for energy storage applications and carbon sphere as dopants for PANI to retain its electroactivity at neutral pH values. With this background the work undertaken in this thesis entitled **"Synthesis of Electroactive Nanocomposites for High-Performance Energy Storage and Beyond"** is presented in the form of following four chapters.

Chapter 1: Introduction to Energy Storage devices, Graphene, Spinel Oxides and Polyaniline for Supercapacitors and Electroactivity of Polyaniline at Neutral pH

This chapter is an introductory part that of the thesis which gives an overview on energy storage devices, importance and types of supercapacitors. Various materials used for supercapacitors such as graphene, spinel oxides, conducting polymers especially polyaniline and various polyaniline based nanocomposite materials for supercapacitors. This chapter also explains importance of electroactivity of polyaniline at neutral pH. Brief introduction to carbon spheres.

Chapter 2: Synthesis of Polyaniline-β-Cyclodextrin-Graphene Nanosheet Triad and Radical Cation Stabilization of Polyaniline: Performance Evaluation for Energy Storage Application

This chapter deals with the synthesis of supramolecular polyaniline-β-cyclodextrin-graphene nanosheet (PANI-β-CD-GNS) triad using graphene oxide (GO) and presynthesized PANI-β-CD. The microstructure and morphology of the triad are characterized by various techniques. The enhanced radical cation stabilization of the triad after conjugating with graphene is confirmed by electron paramagnetic resonance (EPR) spectroscopy. Then, the synthesized triad is tested for its energy storage application, it showed excellent specific capacitance of 567 F g^{-1} at 2 mV s^{-1}, good long term cycling stability with 88.5% capacitance retention after 1000 consecutive charge-discharge cycles at 5 A g^{-1}. This triad also exhibited high specific energy density of 31.8 Wh kg^{-1}, and high power density of 5061 W kg^{-1}.



Chapter 3: Copper Chromite-Polyaniline Nanocomposite for Energy Storage Application

In this chapter, we report a novel copper chromite-polyaniline ($CuCr_2O_4$-PANI) nanocomposite electrode material for fabrication of high-performance supercapacitor. First $CuCr_2O_4$ is synthesized via sol-gel driven epoxide method followed by its nanocomposite with PANI through in situ chemical oxidative polymerization method. The synthesized nanocomposite is characterized by FTIR, EDAX, BET surface area measurement, XRD, SEM and XPS. Then, $CuCr_2O_4$-PANI nanocomposite is investigated for its energy storage application using cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and galvanostatic charge-discharge (GCD) tests. $CuCr_2O_4$-PANI nanocomposite exhibited the best capacitance compared to individual components

and it showed the highest specific capacitance of 535 F g^{-1} at 2 mV s^{-1}. Further, this nanocomposite showed excellent long cycle life with 90.3% retention of its specific capacitance at 5 A g^{-1} and showed the highest specific energy density of 13 Wh kg^{-1} at 0.1 A g^{-1} and high power density of 2926.8 W kg^{-1} at 10 A g^{-1}.

Chapter 4: Carbon Sphere-Polyaniline Nanocomposite: Retention of Electroactivity at Neutral pH

In this chapter, we have demonstrated a novel strategy to retain electroactivity of polyaniline (PANI) using inherently fluorescent carbon spheres (IF-CSP) as a doping agent by making nanocomposite (IF-CSP@PANI) through in situ chemical oxidative polymerization of aniline in presence of IF-CSP. The synthesized composite was characterized by FTIR, UV-Vis, FE-SEM, EDX, XPS, XRD, TGA and zeta potential studies. IF-CSP@PANI showed excellent electrochemical activity than PANI in neutral media at pH 7.4 with high cycling stability which was confirmed by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). Additionally, we have investigated biocompatibility of the nanocomposite using MTT assay and due to intrinsically fluorescent property of carbon spheres in the nanocomposite, cellular uptake study also carried out using confocal laser scanning microscopy (CLSM).

Future scope of the work is discussed briefly at the end of the thesis.