Integration of nanomaterials for photovoltaic energy generation and storage

Synopsis by: Mini P A, Reg.No. KH.NS.D* NMS08006

Chapter 1: Introduction

Solar energy, the major renewable energy source, has the potential to become an essential component of future global energy production. Dye sensitized solar cell (DSSC) [1], a third generation photovoltaic cell, represents one of the most promising of several alternatives a cost effective concept for solar to electric energy conversion that has been offered to challenge conventional silicon solar cells [2] over the past two decades. To date, an overall power conversion efficiency of greater than 11% has been reported for DSSC’s [3]. Although the maximum achieved efficiency in DSSC is shrunk in comparison to that achieved for silicon solar cell (efficiency of 25%)[4] and thin film solar cell (efficiency of 19.9%)[5], the DSSC has the lowest cost input between $1.00 and $2.83/Wp (Under the assumption of 5% efficiency) [6] and functions very well even under diffuse light conditions. The DSSC has a simple construction and is made with low cost nanomaterials thus making it amenable to a roll-to-roll mass scale printing/manufacturing process [7].

In DSSC, a monolayer of dye molecules (sensitizer) absorbs the incident light giving. Upon light absorption, the electron in dye ground state (S) is promoted to an electronically excited state (S*) from where it is injected into the conduction band of a large band gap semiconductor film (TiO₂). The electrons are transported through the TiO₂ film by diffusion before reaching the anode of the cell (SnO₂:F coated glass substrate) and the external circuit. The positive charges (holes) resulting from the injection process are transferred into a liquid electrolyte by reaction of the dye cation (S⁺) with the reduced species of the redox couple in the electrolyte solution. This leads to the regeneration of the charge neutral state of the sensitizer. The most typical redox couple is I⁻/I₃⁻. After ionic diffusion, the carrier of the positive charge, that is I₃⁻, reaches the cathode, where it releases its charge, thus being reduced back to I⁻. The latter process typically requires a catalytic amount of platinum on the cathode surface. Overall, the photoconversion process is regenerative; that is, there is no net change in the chemical composition of the cell. The schematic is shown in Figure 1. To store generated electrical power from any photovoltaic unit, another device such as a secondary battery [8] becomes necessary. However, repeated oxidation and reduction cycles shorten the lifetime of batteries. Conventionally, a secondary battery is used to store electrical power, which provides high energy density. Rechargeable batteries use electrochemical reactions that are electrically reversible.

Figure 1: Principle of operation of the dye-sensitized solar cell
Commonly used secondary cell chemistries [9] are lead acid, nickel cadmium (NiCd), nickel metal hydride (NiMH), lithium ion (Li-ion), and lithium ion polymer (Li-ion polymer). Most batteries require 3-8 hours to recharge completely and maintain their required cycle life. Voltage excursions outside its operating range can cause irreversible changes in its crystal structure and damage cell operations. So the capacitor is a more desirable tool than rechargeable batteries due to its longer lifetime, larger cycling capability, possibility of fast recharging, large temperature range and environmental compatibility. Conventional capacitor consists of two conductors separated by a dielectric layer [10]. When a potential difference (voltage) exists across the conductors; an electric field develops in the dielectric due to polarization. This field stores energy, which can be slowly charged and discharged quickly to provide large amount of energy in a short pulse. They have relatively less energy density but high power density [11] compared to batteries. A super capacitor [12] is a more desirable device due to its reasonable energy density and stable operating characteristics. Super capacitors are governed by same principle as that of capacitor; however they incorporate high surface areas and much thinner dielectric. Super capacitors are classified into three broad categories (depending on the charge storage mechanism and material used).

**Faradic mechanism of charge storage – Pseudocapacitors:** This class of super capacitors uses those materials, which can undergo faradic reactions in order to store charges. It is through these faradic reactions that charge transfer occurs between the electrode material and the electrolyte (electrosorption, reduction-oxidation reactions, and intercalation processes) [13-14]. Different materials used for pseudo capacitors are conducting polymers like poly(pyrrrole), PEDOT, poly(acetalyne) and metal oxides (NiO,RuO$_2$,MnO$_2$ etc).

**Non-faradic mechanism of charge storage --Electrical Double Layer Capacitors (EDLC):** EDLCs are constructed using two carbon-based electrodes, with a separator and electrolyte. Advantages of EDLCs are that they can provide high power capability, relatively high energy density, excellent reversibility and long cycle. Also they exhibit 20–200 times larger specific capacitance than conventional capacitors [15-16]. EDLCs offer good operational voltage range of 2-2.5 V. Energy is stored in EDLC as charge separation in the double-layer formed at the interface between the solid electrode material surface and the liquid electrolyte in the micro-pores of the electrodes.. Electrode materials used are graphene, carbon aerogels, carbon xerogel, carbon nano fiber, carbon nano tube.

**Hybrid capacitor:** These type of capacitors utilizes the properties of both EDLC and pseudo capacitor, i.e., they use both faradic and non- faradic reactions for energy storage without losing the cycling stability. Materials used are carbon-conducting polymer composites. Outstanding challenge for direct solar energy storage is to invent a device incorporating both photovoltaic and storage functions in a single cell structure. A self-rechargeable photovoltaic cell [17-18], which can directly store the electric energy generated by light, has been studied and is becoming a research spotlight in solar energy science and photovoltaic (PV) industry. To ensure in-situ electric storage function, structurally, a photocell should possess solid-state dielectric/electrochemical interfaces where photon energy is converted to polarized charge/electrochemical potential. A photo-rechargeable device enables conversion of spectrally varying light to stable electric energy. In this respect, efforts have been made to combine a photovoltaic electrode and electric double layer-active materials for direct storage of light energy. The photocapacitor, being capable of cyclic charge–discharge with a charging voltage of 0.45 V, achieved a capacitance per unit area of 0.69 F cm$^{-2}$ [17]. An improved structure of a high-voltage photo-rechargeable capacitor in three-electrode configuration, comprising a dye-sensitized mesoporous TiO$_2$ electrode, two carbon-coated electrodes, and two liquid electrolytes, attained a storage voltage of 0.8 V and energy density per area of 47 µW h cm$^{-2}$ [19]. This photo-capacitor is able to store efficiently but independent working of the solar cell and capacitor is not possible. Once the capacitor is fully charged, further photon
to electron conversion is not possible. This means that solar part is not independent in function and so the capacitor has to be drained for further storage. Other principal deficiencies of the photocapacitor include an incomplete (and hence inefficient) operation of the Gratzel cell cycle [20] and the use of micron-sized carbonaceous materials for the storage component with limited charge storage capacity.

To address these challenges, we have progressively evolved a novel DSSC-supercapacitor integrated structure [8] that can fulfil the above requirements. This integrated structure includes nano-structured DSSC and different forms of supercapacitor structures having different energy and power density. This stores energy simultaneously and efficiently upon photo generation, and enables material level implementation of the dual functions of electricity generation and storage. A direct storage thin film cell enables the incorporation of a thin photocell (DSSC) capable of electrical generation and integrating it with a storage cell minimizing circuitry and diminishing the electrical losses due to circuitry. The device is capable of repeated photo-charge and discharge. A merit of this device is that both generation and storage part is capable of functioning independently so that photovoltaic unit and storage units can be independently optimized by changing the materials to maximize the performance. The Gratzel cell is completely operational thus maximizing generation and storage efficiencies. Novel nanomaterials such as a network of carbon nanotubes, graphene, composites of carbon nanotubes and graphene have been used to deliver high performance storage units with a storage capacity of up to 1 F cm⁻².

**Objectives of this study**

The specific goals of this study are:

1. To prove the concept of integration of dye sensitised solar cell and storage supercapacitor in a single physical device and optimize working configuration.
2. To understand the basic physics of operation of the integrated device of DSSC with the supercapacitor.
3. To develop dielectric based solid state capacitor with nanosized ZrO₂ and BaTiO₃ and determine their suitability for integration with the DSSC
4. To develop conducting polymer, chemically modified carbon nanotube networks, chemically modified graphene networks and conducting polymer-carbon (activated carbon/carbon nanotubes/graphene) composite capacitors having reasonable power and energy density and determine their suitability for integration with the DSSC.
5. To design and develop different supercapacitor configurations so as to achieve high operating voltages and hence higher energy density.
6. To conduct studies on the integration of the optimized supercapacitor with an optimised reference energy generating unit (DSSC).
7. To design and develop different supercapacitor configurations so as to achieve high operating voltages and hence higher energy density.

**Chapter 2: Proof of Concept - Upon photo illumination of a Dye Sensitised Solar Cell (DSSC), electrical energy can be stored directly to a capacitor, which is integrated to the Dye sensitized solar cell**

Conventionally solar cells are used in conjunction with battery systems to effectively utilize them as reliable sources of power. Recently, new approaches have been investigated whereby separate battery systems may be avoided or at least partially replaced. One such approach has been the introduction of thin film photo-charged capacitors [17-19]. Even though the reported system stores energy, the disadvantages are: independent working as a solar cell and a capacitor is not practically possible. Once the photo-capacitor is fully charged further light exposure is not converted into energy, the capacitor has to be drained for further energy storage. Other principal deficiencies of the photocapacitor include an incomplete (and hence inefficient) operation of the Gratzel cell cycle [20] and the use of micron-sized
carbonaceous materials for the storage component with limited charge storage capacity. Our proposed innovative system eliminates these major drawbacks by providing independent working schemes for both the capacitor and the solar cell.

Figure 2: Schematic diagram of integrated solar cell with capacitor

The integration scheme is shown in Figure 2 which is basically a DSSC coupled with ZrO₂ dielectric based capacitor. In this scheme, the heart of the integration is TiO₂-Ti-TiO₂ double anodized layered structure (DALS), which separates the photovoltaic (PV) component from the storage component of the integrated device. On one side of the DALS the device contains the dye and electrolyte and counter electrode of the PV component. On the other side of the DALS is a solid-state zirconia dielectric layer to act as a capacitor component followed by a single side anodized Ti layer (SALS) (TiO₂-Ti). DALS acts as independent electrodes for both the PV and the capacitor while the SALS act as the electrode for the capacitor.

Brief explanation of charge workflow in the integrated cell: Illumination of the solar cell generates electrons, which are first injected into the TiO₂ semiconducting layer of the DALS and flows along the length of the nanotube to the common Ti plate of the DALS. From here, the provided voltage is adequate to cross the potential barrier (schottky barrier) created by Ti-TiO₂ interface, the electrons are driven into the TiO₂ layer of the DALS and are absorbed at the high surface area TiO₂/zirconia interface. The photogenerated hole migrates through the electrolyte and reaches the counter electrode (platinized ITO) of the DSSC and further travels along the external connection to the Ti plate of SALS. On exceeding the schottky barrier, the hole starts to flows from Ti plate to TiO₂ nanotubes of SALS. Platinum coated counter electrode (ITO) of solar cell, which is connected to the SALS of the capacitor accepts electrons from Ti to replenish the electrolyte; hence Gratzel cell is complete in its work flow. Anodization technique was used to create TiO₂ nanotube on Ti plate carried out in hydrofluoric acid (HF)/dimethyl sulfoxide (DMSO).

Figure 3: SEM images of double side anodized TiO₂ nanotubes

Figure 3 shows the SEM image of double side anodized titanium plate where it is clearly visible that nanotubes have grown on either side of Ti plate. One side of DALS was sensitized with eosin dye and a thin dielectric layer of ZrO₂ was deposited on the other side (this forms the capacitor). Lithium iodine/ iodide in ethylene glycol was taken as the
electrolyte and SALS is assembled on top of the ZrO$_2$ layer to complete the capacitor structure. 

**Device characterization of isolated DSSC, Capacitor cells and integrated cell:** Initially, the solar cell and capacitor were characterized separately and then photo-charging and discharging of an integrated device was carried out. Charging and discharging of capacitor with (48hrs anodization) separately (without integration) is carried out at a constant current (10µA/cm$^2$) and capacitance of 140 µF/cm$^2$ is obtained (Figure 4(b)). A potential difference was applied between the Ti and the TiO$_2$ nanotube layer on an anodized plate and the resulting current output through the Ti/TiO$_2$ interface was measured. The threshold voltage at which a measurable current was obtained was equivalent to the schottky barrier potential. The I-V curve is shown in Figure 4(a) which indicated a barrier breakdown voltage of 0.26 V, which in this case was lower than the open-circuit voltage of the PV ($V_{oc}= 0.42$ V, $J_{sc}= 970$ µA cm$^{-2}$, $V_m=0.33$ V, $I_m=660$µAcm$^{-2}$). The I-V curve for the DSSC is shown in figure 4(d).

Before the combined device was exposed to light, the counter electrode of solar cell is connected to the SALS of capacitor. Upon illumination charges generated in the PV section are stored in the capacitor leading to an increase in the capacitor voltage as shown in Figure 4(c). The solar cell was illuminated for 100 seconds by connecting it parallel with capacitor as shown in figure 2, and then disconnected (i.e. the counter electrode of solar cell is disconnected from the SALS of capacitor) and voltage across the capacitor was noted for 1500 seconds in the dark and found that voltage remains constant. When discharged by an external current of 1 µA/cm$^2$, an initial rapid discharge rate was observed which was followed by a slower discharge at longer times. This proves the integrated functioning of the PV and storage components of the integrated device.

**Development of nanosized ZrO$_2$ and BaTiO$_3$ for dielectric capacitors:** Hydrothermal process was found to be most preferable because in this method crystal size can be controlled and miniaturized by altering the process conditions. Hydrothermally processed BaTiO$_3$ and ZrO$_2$ give more control over film thickness and reproducibility in a capacitor. Commercially purchased ZrO$_2$ was taken in a 10 M NaOH aqueous solution and it heated in hydrothermal reactor at 120°C for 48 hours. Obtained nanosized ZrO$_2$ was used as dielectric layer between two TiO$_2$ nanotubes based electrodes and maximum obtained capacitance is 100 µF/cm$^2$. BaTiO$_3$ was synthesised hydrothermally in two methods; **Ex-situ** method: 2 M solution of barium hydroxide and 1.0M TiO$_2$ was added heated in a hydrothermal reactor at 300°C for 4 hours. **In-situ** method in which anodized Ti plate act as the TiO$_2$ precursor which is dipped in

![Figure 4](image-url)
Ba(OH)$_2$ in hydrothermal container and processed. Ex situ method provides free suspension of BaTiO$_3$ in acetonitrile, where as in situ method dissolves TiO$_2$ nanoube and precipitates BaTiO$_3$ on Ti plate.

**Figure 5:** (a) SEM image of BaTiO3 prepared by Ex-Situ method (b) Charging discharging at constant charging and discharging current of 3µA/cm$^2$

The capacitor assembled with BaTiO$_3$ by In-situ method showed lesser capacitance (62µF/cm$^2$) compared to the capacitance (500µF/cm$^2$) with BaTiO$_3$ by Ex-Situ method. SEM image is shown in figure 5(a) and figure 5(b) shows the charging-discharging at constant current. Best performing BaTiO$_3$ capacitor is integrated with solar cell and its photocharging and discharging studied. When discharging is studied, an initial voltage drop followed by a slow decay is found. During charging a voltage develops across capacitor upon illumination, the voltage remains constant until a discharging current is applied. Once discharging current is applied voltage starts to drop or capacitor starts to discharge. Also, nature of the voltage charge curves show an almost vertical slope with very little time-dependant portion. This indicates a much superior polarizability of the nanosized-BaTiO$_3$ dielectric when compared to nanosized ZrO$_2$.

**Chapter 3: Development of conducting polymer/graphene composites for energy storage**

Organic conducting polymers such as polyaniline, poly(pyrrole), poly(thiophene) etc., have been extensively studied due to their electrical conductivity, cost effectiveness and ease of synthesis [21]. The reduction – oxidation capability of conducting polymers rendered them as good candidates for capacitive electrodes. We developed a composite electrode of two different conducting polymers poly(pyrrole) and PEDOT (Poly(3,4-ethylenedioxythiophene) with graphene; which showed high electrical storage capacity and good stability. In the present study, we used graphene nanolayers as a scaffold for electropolymerization of conducting polymers and create a composite electrode for the supercapacitor. Graphene was chosen as a constituent material of the electrode on the account of its high active surface area consisting of large open flat layers and its remarkable electronic transport properties. This composite electrode demonstrated much higher capacitance values [22] than bare polymer electrode and also shows good stability under repeated cycling.

The initial step for making composite electrode is the electrophoretic deposition (constant voltage of 15 V applied for 600 sec) of graphene on Ti/ITO plate and on top of which a thin layer of polymer (either poly(pyrrole) or PEDOT) is deposited by electropolymerization. Electro-phoretically deposited graphene electrode was taken as the anode for the polymerisation. This structure is a porous 3D network, which has better porosity than bare polymer film and hence entire volume of the electrode would contribute for the capacitance.

**Synthesis and characterization of poly (pyrrole)/graphene composite electrode**: Bare poly(pyrrole) (PPY) electrode is prepared on polished Ti plate by electropolymerisation of pyrrole (at constant current of 1 mA), carried out by taking Ti plate as the anode. This resulted in an adhesive polymer film on Ti plate. Figure 6(a) and (b) shows the SEM image of bare poly (pyrrole) film on Ti plate; which is a uniform 2D film. Cyclic voltammetry (CV) is
carried out in 0.1 M LiClO$_4$ to find out the capacitance, the specific capacitance is computed from the CV curve as follows:

$$C = \frac{I}{(dV/dt)}$$

Where, $I$ is the current corresponding to the reduction peak in the voltammogram and $dV/dt$ is the voltage scan rate in volt/second.

Time of polymerization of the pyrrole monomer on bare substrate is varied from 500 to 1500 seconds and maximum area capacitance of 47mF/cm$^2$ is obtained for 2500 sec. And the corresponding maximum specific capacitance is 190F/g (Figure 6(e)). It was also studied as to how the amount of polymer on graphene affects the performance of the capacitor. This is carried out by varying time of polymerization. Composite electrode was prepared by the electro polymerization of pyrrole on graphene coated Ti plate. The time of polymerization varied from 50 to 3000 seconds and found that optimum time of polymerization to get maximum area capacitance is 1500 seconds and corresponding area capacitance is 151 mF/cm$^2$ and specific capacitance 1510 F/g. SEM clearly shows that composite electrode structure is highly porous compared to polypyrrole electrode (Figure 6(c) and (d)); this porosity enhances the electrode interaction with the electrolyte, hence the increase in capacitance. Apart from providing nucleation centers for polymerization, the graphene layer functions as a mesh of tiny current collectors, which facilitates rapid charging and discharging cycles.

**Figure 6:** (a) and (b) shows SEM images of bare poly(pyrrole), (c) and (d) shows SEM images of composite of Graphene-Polypyrrole, (e) shows the CV of Graphene/Poly(pyrrole), composite electrode at a scan rate of 10 mV per second, (f) shows the variation in area capacitance with time of polymerization of pyrrole, (g) cycling of PPY electrode, (h) cycling of Graphene/PPY electrode.

From the figure, figure 6(e) shows the improvement in oxidation and reduction current upon composite formation. The capacitance of the graphene/Ppy composite films deposited at different polymerization times is studied using CV and graph showing variation of area capacitance with polymerization time was plotted (Figure 6(f)), which shows the area capacitance as a function of polymerization time. Figure 6(e) shows the enhancement in capacitance for composite electrode, wherein it compares the CV of bare PPY, graphene and graphene + PPY composite. This clearly shows composite electrode has maximum area capacitance. Figure 6(g) and (h) shows the cycling (25 cycles) PPY and Graphene/PPY, which clearly shows the improvement in stability upon composite formation. Electro polymerization of pyrrole proceeds by successive addition of units to the polymer chain backbone; beyond the optimum time of polymerization it adversely affects the capacitance (Figure 6(f)). As the time increases above the optimum value, densification of polymer happens which would close the pores of electrode and minimize the accessibility of electrolyte, hence the capacitance decreases. Maximum area capacitance of 151 mF/cm$^2$, volume capacitance of 151 F/cm$^3$ and specific capacitance of 1510 F/g were obtained for a scan rate of 10 mV/sec for the sample polymerized for 1500 sec. The energy density is found to be 5.7 Wh/kg, and the power density computed is 3 kW/kg.
Synthesis and characterization of PEDOT/Graphene composite electrode: PEDOT, a highly stable p-type conducting polymer was selected to develop a composite electrode with graphene. We could demonstrate much higher specific and area capacitance values when compared to literature and a thin film of PEDOT. Normally the main advantage of these hybrid electrodes over the conducting polymer electrodes is that these composites have been able to achieve superior cycling stability comparable to that of EDLCs while retaining the high storage capacity of faradic electrodes. Graphene-PEDOT composite electrodes are also suitable for supercapacitor applications; fabrication technique is electrophoresis of graphene (15V, 600 sec) followed by electro-polymerization. Figure 7 (a), (b) shows the AFM of PEDOT having a thickness (~ 600 nm) and Figure 7(c) and 7(d) shows the SEM images of PEDOT and its Graphene composites The PEDOT/graphene composite electrode also showed excellent electrochemical stability in repeated CV studies (Figure 7(f)). Here also, the capacitance is found to be a function of time of polymerization and maximum capacitance is obtained for 8 minutes. The composite electrodes show median specific capacitance of 1410 F g⁻¹ and area capacitance of 199 mF cm⁻². In this chapter, we could show the successful synthesis and characterization of high performance supercapacitive electrodes composed of graphene/Ppy and Graphene/PEDOT composites. Such electrodes have yielded high values of mass specific capacitance, area capacitance. This work can be extended to include many other polymers belonging to the conducting polymer family. Possible applications include high-density supercapacitors, photovoltaic cells and other energy storage applications.

Figure 7: (a) and (b) shows the AFM images of electro-polymerized PEDOT,(c) and (d) shows the SEM image of PEDOT /Graphene (e) CV of PEDOT/Graphene(f) cycling of PEDOT/Graphene electrode

Chapter 4: Development of super-capacitor electrodes with various forms of carbon and its polymer derivatives

This study shows the development of an entangled network of nano-carbon, which is chemically modified for high capacitive electrodes. This work deals with how the chemical modification of activated carbon, graphene, carbon nanotubes by the introduction of faradiac constituents like metal oxide or a conducting polymer improves the effective capacitance. The mechanism for energy storage is based on a combination of fast faradiac reactions between electrode materials and electrolyte, which contributes to the “pseudo” capacitance and pure “double layer” capacitance; contributed by the carbon allotropes. Thus the developed system is a hybrid capacitor. The faradic components are NiO and poly(pyrrole).
Detailed study on the specific capacitance, cycling stability, charge-discharge of hybrid capacitor electrode materials in both symmetric and asymmetric configurations was carried out. The key factors determining the performances of electrochemical capacitors are specific surface area, porosity, properties of electrolyte and these properties are crucial in achieving high energy and power density.

In electric double layer capacitors (EDLCs), the sizes of cation and anion of the electrolyte are important factors in the adsorption of the ions into the pores of the carbon-based electrodes. EDLCs store the electric charge directly across the double layer of the electrode [23], since the carbon forms a porous structure allowing sites for the electrolyte ions to pass through. This is termed as a true capacitance effect since there is no charge transfer across the interface. In certain cases, surface charges can be produced due to the surface dissociation, ion adsorption from the electrolyte and crystal lattice defects. The capacitance contributed by EDLC is similar to that of a parallel plate capacitor. If an excess or deficit of ions is produced at the electrode surface, counter ions in the electrolyte build up near the surface of the electrode, so as to offer electro neutrality [24].

It was already reported that the operating voltage of a capacitor depends on the nature of electrolyte (specifically on decomposition voltage of electrolyte) [25-26]. Aqueous based electrolyte showed lesser operating voltage compared to organic based electrolyte.

**Aqueous electrolyte:** In the first case, small quantity of NiO on the carbon electrodes under goes an electrochemical reaction with the ions present in the electrolyte. Here aqueous KOH is taken as electrolyte and reactive species in electrode (NiO) reacts with OH$^{-}$ ions and under goes redox reaction in the appropriate potential window.

\[
\text{NiO} + \text{OH}^{-} \rightarrow \text{NiOOH} + e^{-}
\]

By this reaction charges can be admitted or released from the electrode to the external circuit through electrode/electrolyte interface.

**Organic electrolyte:** In the second case, carbon/conducting polymer composites are formed by the electro polymerization of pyrrole on electro-phoretically deposited carbon-based substrate. An interconnected network of carbonaceous material provides a high surface area and exhibits double layer capacitive effect. This network also functions as a highly conducting template for polymerization of pyrrole, which undergoes faradiac reaction in organic based LiClO$_4$ electrolyte.

**Activated carbon/NiO Hybrid capacitor:** Activated carbons produced by acid treatment of ball-milled carbon with which causes exfoliation of carbon due to the negativity of the nitrate ions in the acid and the intrinsic negative charge of carbon. Generally they have specific surface area of 800-1500 m$^2$/g, which allows many sites for electrolyte interaction. This type of activated carbon has very fine pore size. Here the surface area of the carbon plays an important role in capacitance, if the specific surface area is greater, the higher the specific capacitance. Because of these defects that are produced in the carbon due to acid treatment and milling results in activation of the carbon. An electrophoretic bath was prepared with 5 mg of activated carbon ~100nm with 0.4 mM Ni(NO$_3$)$_2$ in iso-propanol and is ultrasonicated. Upon electrophoretic deposition (15V, 600 second), activated carbon gets deposited over cathode because of the Ni$^{2+}$ ions. When this electrode is annealed in oxygen atmosphere; Ni$^{2+}$ coated on activated carbon gets converted to NiO, which is the active faradic capacitive component on carbon. Depending upon milling time size of activated carbon can be varied. Here in this study, we have constructed hybrid capacitor electrode having high specific capacitance with different sized carbon and nickel oxide. Maximum specific capacitance is obtained is 1072 F/g at 100 mV/s and area capacitance of 0.488 F/cm$^2$ (for ball-milled size < 100 nm with chemical activation).

**Synthesis of Graphene/NiO and CNT/NiO hybrid supercapacitors in aqueous electrolyte:** An electrophoretic bath was prepared with 5 mg of CNT with 0.4 mM Ni(NO$_3$)$_2$ in iso-propanol and is ultrasonicated for 1 hour to get a uniform distribution of CNT
decorated by Ni$^{2+}$ ions. Upon electrophoretic deposition (15V, 600 second), CNT gets deposited over cathode because of the Ni$^{2+}$ ions. When this electrode is annealed in oxygen atmosphere; Ni$^{2+}$ coated on CNT gets converted to NiO, which is the active faradic capacitive component on carbon. Similar procedure is followed to get chemically modified graphene. Figure 8(a),(b) shows electro-phoretically deposited CNT and graphene respectively. Capacitance of the electrode is measured with CV study.

0.1 M KOH in aqueous medium is taken as the electrolyte. A potential window of -1.5 to 1.5 V is applied. From the CV (Figure8(c)), the single electrode capacitance is calculated and chemically modified CNT showed maximum area capacitance of 799 mF/cm$^2$ for 60-minute electrophoretic deposition. Graphene showed maximum area capacitance of 466 mF/cm$^2$ for 50-minute electrophoretic deposition. Charging and discharging of symmetric supercapacitor is carried out at constant current [Fig 8((d),(e))]. The operating voltage is ~ 2 to 2.3 V (for both CNT and graphene); graphene based electrodes show a more controlled discharge.

**Figure 8** (a) shows the SEM of CNT on Ti (b) Shows the SEM image of Graphene (c) Cyclic voltammetry of CNT in 0.1M KOH (d) and (e) shows the charging and discharging of CNT and Graphene in KOH respectively (f) Variation in area capacitance of graphene with EPD deposition time.

**Synthesis of CNT/PPY composite electrode supercapacitor in organic electrolyte:** Composite electrode Figure 9(a), is prepared by electrophoresis (at constant voltage -15V) of CNT followed by electro-polymerization (at constant current 1 mA) on Ti plate and 0.1 M LiClO$_4$ was taken as the electrolyte. The area capacitance and specific capacitance of single electrode was calculated from CV (Figure 9(b)) and is found to be 420 mF/cm$^2$, 508 F/g. Symmetric composite electrode super capacitor is assembled and it’s charging discharging studied (figure 9(c)). It charges to very high voltage (7-8 V), but once after reaching the maximum voltage, the voltage fluctuation occurs across the supercapacitor. Apart from the voltage fluctuation, the IR drop is found to be very high; the voltage finally settles down to 2 -3 V. Even though the voltage is high, it is unstable to use for a practical application. Finally, we tried to couple the advantages of both bare carbon (renders stability) electrode and CNT-polymer (yields high voltage) composite electrode through an asymmetric battery type hybrid capacitor construction, i.e., one electrode is CNT and other one is CNT/PPY. We were able to obtain a highly stable supercapacitor, which can charge up to 7 V and can finally store 4.1 V (after the IR drop) as shown in Figure 9(d). Energy density and power density is calculated 390 Wh/kg, 36 W/Kg. Thus, we were able to develop a super capacitor having high voltage capacity and stability in asymmetric configuration. In this configuration, both
CNT in KOH and CNT/PPY in LiClO₄ may undergo simultaneous charging and discharging; this would provide high voltage storage. Table 1 shows the voltage capacity and energy/power densities of super capacitors in different configurations.

**Figure 9:** (a) and (b) SEM images of CNT/PPY composite electrode (c) Charge and discharging of CNT/PPY symmetric electrode (d) Charge-Discharge of CNT-CNT/PPY asymmetric capacitor

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</table>

Table 1 Shows the capacitance and operating voltage variation with electrode.

**Integration of CNT and CNT-PPY capacitor with solar cell:** Last part of this chapter shows the implementation of supercapacitor with solar cell. Both DSSC and silicon solar cell (commercially available) were used as the electricity generator. We have already seen the operating voltage of CNT/KOH capacitor is 2.3 V hence single DSSC (Voc is < 0.7V) can’t utilize the maximum storage efficiency of this capacitor hence we need to develop a practical DSSC panel with three DSSC cells in series. Similarly symmetric CNT/LiClO₄ capacitor and asymmetric battery type hybrid capacitor require very high solar voltage source to charge it completely. CNT – KOH supercapacitor, which showed maximum area capacitance, was selected to combine with DSSC. The output of the solar cell is fed to the CNT based symmetric supercapacitor and photo charging and discharging of an integrated DSSC with CNT – KOH supercapacitor)) is shown (figure 10(a)). Around 80% of Voc is found to be stored in supercapacitor. The equivalent circuit model of this integrated structure is a solar cell is in parallel with a capacitor. When illumination starts, the voltage across the supercapacitor rises to maximum value. As long as illumination is on, the voltage remains at the maximum value. When illumination turns off, the voltage initially reduces and stabilizes. The internal resistance of the supercapacitor causes an initial IR drop and around 20% of Voc drops; remaining 80% gets stored in the supercapacitor. Figure (10(b)) shows the voltage variation in DSSC/CNT based supercapacitor-integrated structure. Solar cell is illuminated for 100 seconds and it is found that Voc =0.57 V and ~ 0.45 V gets stored in the
supercapacitor. The supercapacitor retains this voltage until a discharging current is applied. A discharging current of 10 µA is applied after 400 seconds; then the voltage across the capacitor has dropped to 0 V in 65 seconds.

![Figure 10: Photo-charging of CNT/KOH symmetric capacitor from DSSC (a) voltage variation across the capacitor (b) Voltage variation while discharging current of 10µA current applied.](image)

**Chapter 5: Conclusion and future aspects**

In conclusion, we were able to prove the concept of integration of photovoltaic energy generator (DSSC) with a storage device in a single thin film layer. Initially, capacitor with two different nanosized dielectric materials, ZrO2 and BaTiO3 is developed and maximum capacitance obtained is 500 µF/cm². To further enhance storage capabilities, we developed faradic supercapacitors with conducting polymers (poly(pyrrole) and PEDOT) and their hybrid composites with graphene. We were able to obtain a significant increase in supercapacitance with area capacitance of the order of 100 to 200 mF/cm². Research was also conducted to develop another set of carbon-based hybrid composite supercapacitors (activated carbon with nickel oxide, carbon nanotubes with poly(pyrrole), carbon nanotubes with nickel oxide, graphene with nickel oxide); maximum area capacitance is showed by CNT-Nickel oxide (800 mF/cm²) with an operating voltage of 2.2V. CNT/PPY supercapacitor electrode showed reasonable capacitance, higher operating voltage but lesser stability. An Asymmetric battery type hybrid capacitor with CNT /NiO and CNT/PPY was in two electrolyte system were developed, which is capable of high operating voltage (4.1V) with good stability. Integration efforts were directed by combining the best performing supercapacitor with DSSC solar cell showing almost 80% of energy storage. It was also demonstrated that integration is not limited to DSSC alone. Very high voltage capacity capacitors were developed which can be integrated with high efficiency solar cell for the maximum energy conversion and storage.

This study shows the easy method of development of high capacitive composite supercapacitor electrodes using cheap raw materials like carbon and polymers. Prospects for further study include an efficient design of an integrated solar cell/storage panel with associated electronic circuitry and investigations into effective packaging and circuitry schemes.