Chapter 1

Introduction
The delicate balance in the energy-environment relationship needs close observation, perpetual consolidation and consistent efforts for improvement. This chapter presents a brief account of the energy-environment relationship and the role of renewable energy and materials in improving this. Initially some of the most viable renewable energy technologies (RETs) having largest impact on this relation have been identified. Carbon nanotube, one of the well-known potential materials with high prospect of influencing the future course of development of the identified renewable energy technologies, has been thoroughly explored. The rationale of the thesis was formed after reviewing the current literature on its synthesis and on discovering the possibility of use of green precursors for this. Subsequently on the basis of a detailed analysis of the possibility of specific applicability of these carbon nanomaterials in the identified renewable energy technologies the aims and objectives of the work have been set. Finally this chapter concludes with the outline of the thesis.

1.1. Impact of materials on energy, environment and sustainability

Materials have always played significant role for sustainability of development of civilizations through the ages. Progress made by civilizations has been associated with the discovery, development, and use of new materials. Very recently the functionalities of these materials have been redefined with the discovery of their nanoforms. These materials have been identified to be capable to address many of the present day global challenges related to energy and environment. The growing energy demand and the associated environmental problems converge towards global unsustainability. In addition to this the instabilities due to the geopolitical confinement of fossil fuel reserves poses a imminent threat to energy security and unconfined nature of environmental problems challenges the very existence of the most of the nations including India. Renewable energy (RE) technologies have great potential to achieve sustainability and can address both energy security and climate change issues.
Although most of the renewable energy technologies are quite mature but the constraints like efficiency and cost could not bring many of these to the level of commercialization. Use of nanomaterials in such RE systems has shown encouraging results in a number of RE technologies. In the current scenario, research, development and application of some of the important nanomaterials for the most potent RE technologies is the basic motivation behind the work presented in this thesis. For this availability of the potent RE resources needs to be assessed first, as discussed next.

1.2. Renewable energy resources and potential

Out of all the renewable resources, solar, wind, bio and hydro are the identified potential resources in India. Technologies available for harnessing wind and hydro are now mature and have reached a stage of full commercial exploitation. It may be noted that both are site and region-specific. Now solar and bio-energy resources are uniquely poised. Both are equitably distributed in the tropical regions and both are dependent on materials for their efficient conversion and storage. The conversion technologies for both are also reasonably developed and matured but due to a big role of material science and technology in these there is a vast scope of improvement in the performance of the systems. India being tropical country endowed with these resources naturally [1]. It is pertinent to look for materials with promising characteristics to enhance the performance of the related energy systems and processes. Figure 1.1 shows the potential renewable energy (RE) resources in the globe along with India. It can be seen that India has a major global share of solar and biomass energy resource.

Keeping the resource availability and technologies in mind the present work focuses on the use of carbon nanotubes for these RE technologies.

1.3. Carbon nanotube

A cylindrical tubular nanostructures made of carbon is termed as carbon nanotube (CNT). The tubular structure is made up of graphitic carbon sheets rolled over to form tubular hollow cylindrical structures, it may have single, double and multiple concentric graphitic sheets. Thus depending upon the number of concentric graphene layers CNTs are classified into single-walled carbon nanotube (SWCNT), double-walled carbon nanotube (DWCNT) and multi-walled carbon nanotube (MWCNT).
Chapter 1

1.3

Figure 1.1: Global potential important RE resources, taken from Peter Milson’s report on ‘Overview of RE potential in India’, (GENI, 2006) [2]

Carbon nanotube (CNT), discovered by Iijima in 1991, is an allotrope of carbon just like graphite and diamond [3]. Unlike diamond, where a 3-dimensional cubic crystal structure of diamond is formed with each carbon atom having four nearest neighbours arranged in a tetrahedron, graphite is formed as a 2-dimensional sheet of carbon atoms in a hexagonal array arrangement. Here, each carbon atom has three nearest neighbouring carbon atoms. ‘Rolling’ sheets of graphite into cylinders forms carbon nanotubes. The atomic structure of nanotubes is described in terms of tube chirality, or helicity, which is defined by the chiral vector, \( \mathbf{C}_h \), and the chiral angle, \( \theta \). In figure 1.2, the rolling of the graphite sheet along different axis to form a tube of different chirality is shown. The chiral vector can be described by the following equation:

\[
\mathbf{C}_h = n \mathbf{a}_1 + m \mathbf{a}_2
\]

(1.1)

where the integers \( n \) and \( m \) are the number of steps along the ziz-zag carbon bonds of the hexagonal lattice and \( \mathbf{a}_1 \) and \( \mathbf{a}_2 \) are unit vectors, as shown in figure XX.
The chiral angle (θ) determines the amount of ‘twist’ in the tube. There are two limiting cases where the chiral angle is at 0° and 30°. These limiting cases are referred to as zig-zag (0°) and armchair (30°) based on the geometry of the carbon bonds around the circumference of the nanotube.

1.3.1. Properties of CNT

The CNT due to their distinctive structure and morphology possesses unique physical and chemical properties as tabulated in the Table 1.1. CNTs are considered to be one of the strongest materials known to mankind. The reason for the strength of CNTs is the sp² bonds within the rolled graphite sheets. The Young’s modulus of near perfect SWNTs in the axial direction has been estimated to be 1 TPa [4]. In another study of CVD produced MWNTs the tensile strength was measured to be lower than 100 GPa. Reasons for differences between such estimates and measurements may be due to point defects within the graphite planes and a mis-alignment of the graphitic planes with regard to the central axis. Nanoscale point defects should intuitively have a greater impact on nanotube sized features, versus their micro- and macro-sized fibers. Other more recent research, however has suggested that point and planar defects can act
to strengthen MWNTs as they are strained in the axial direction [5]. SWNTs can be either semiconducting or metallic depending on the chiral vector.

Table 1.1: Some of the important physical properties of CNTs [4-12]

<table>
<thead>
<tr>
<th>Physical property</th>
<th>SWCNT</th>
<th>MWCNT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile strength (Gpa)</td>
<td>50-200</td>
<td>11-63</td>
</tr>
<tr>
<td>Young’s Modulus (GPa)</td>
<td>1000</td>
<td>270-950</td>
</tr>
<tr>
<td>Current density (A/cm^2)</td>
<td>10^7-10^8</td>
<td>10^9</td>
</tr>
<tr>
<td>Electrical conductivity (S/m)</td>
<td>1x10^6</td>
<td>1/13</td>
</tr>
</tbody>
</table>

Besides these, high surface area [13], tunable electrical (both in semiconducting and metallic ranges) and high thermal conductivity [14], are some of the major attributes of CNT, which make them strategic material for some of the RE systems and applications. Thus because of these properties CNTs find applications in RE systems including organic photovoltaic (OPV) cells, fuel cells and supercapacitors. But, the synthesis of CNT has many challenges while still a number of new applications are being proposed. The synthesis and applications of CNTs is being discussed in detail in the following sections of this chapter.

1.3.2. Synthesis of carbon nanotubes

CNT synthesis is one of the focus areas of research for desired quality (such as orientation, diameter, wall thickness, length) and quantity (yield) to address different applications. Since its discovery, several techniques have been reported for their synthesis. Arc discharge [15-16] and laser ablation [17-18] and physical vapour deposition [19] belong to physical techniques whereas chemical vapour deposition (CVD) [20-23] technique is a simple chemical route for synthesis of CNTs. The CNT synthesis techniques differ according to the nature of carbon atomization, which may involve either physical or chemical techniques. Physical technique involves relatively high energy input to the carbon source (precursor) atomization in the form of arc-discharge or laser evaporation [24-26]. Thus, CVD technique is relatively advantageous compared to physical synthesis techniques due to two reasons: i) its ability to be easily modified and scaled-up in terms of quantity of output, and ii) its low energy intensity
processing. But the challenge of the CVD technique lies in the multitude of parameters involved because a small change in the parameters shows remarkable effects on the morphology of the CNTs synthesized [27]. The comparison of CNT synthesis techniques are tabulated in Table 1.2.

The synthesis of CNTs involves transition metal catalysts with high affinity to atomized carbon. Thus the use of metal nanoparticles as a catalyst source to the CVD process is of great interest. The use of nanoparticles and thin films of transition metals as catalyst substrate is a well documented method for the synthesis reaction [28-31]. The success of CVD as a reliable synthesis method for producing commercial quality CNTs requires a detailed, systematic study of all the growth parameters involved in a given synthesis setup.

Table 1.2: Comparison of CNT synthesis techniques [32].

<table>
<thead>
<tr>
<th>Attributes</th>
<th>CVD</th>
<th>Laser Ablation</th>
<th>Arc Discharge</th>
</tr>
</thead>
<tbody>
<tr>
<td>Process temperatures</td>
<td>500-1000°C</td>
<td>3000-4000°C</td>
<td>3000-4000°C</td>
</tr>
<tr>
<td>Carbon source</td>
<td>Solid, liquid and gas</td>
<td>Solid</td>
<td>Solid</td>
</tr>
<tr>
<td>Catalyst type</td>
<td>Particles or thinfilm</td>
<td>Particles</td>
<td>Particles</td>
</tr>
<tr>
<td>Growth surface or collector</td>
<td>High temperature compatible substrate</td>
<td>Copper collector</td>
<td>Carbon rod</td>
</tr>
<tr>
<td>Diameter control</td>
<td>Large distribution</td>
<td>Small distribution</td>
<td>Small distribution</td>
</tr>
<tr>
<td>CNT relative defectiveness</td>
<td>High</td>
<td>Low</td>
<td>Low</td>
</tr>
<tr>
<td>CNT arrangement</td>
<td>Yes, vertical alignment possible</td>
<td>No, randomly arranged</td>
<td>No, randomly arranged</td>
</tr>
</tbody>
</table>

Precursors for CNT synthesis using CVD: Though there is extensive study on yield and quality of CNT synthesized at various synthesis parameters using various precursors, there are some major issues to be addressed a priori, viz., origin and sustainability of
supply of precursors and specific energy intensity of production. The CNT industry currently depends on petroleum based precursors for the synthesis of CNTs. The non-renewable nature of these precursors puts questions on the sustainability of the technology for future production and use. Moreover, the consumption of petroleum based precursors for CNT synthesis is not a carbon neutral process. The CNT synthesis is a high energy intensive process whether it is through physical route (laser ablation or arc discharge) or chemical (such as CVD). As discussed the CVD technique is less energy intensive than the physical techniques and could be scaled up for large scale production, but the scope for improvement to lower the energy consumption needs to be explored.

1.4. **Application of carbon nanotubes in selected RE technology**

The remarkable properties of CNTs resulted in direct and indirect applicability in various RE technologies viz. fuel cell, super-capacitor, catalyst support and organic solar cells. Solar and bio-energy being the most prominent energy resource in India [2], the need, scope, and efforts directed to employ CNTs to enhance the efficiency of these systems is investigated in detail.

1.4.1. **CNT in organic photovoltaic (OPV)**

Sustained research interests have been shown in the development of photovoltaic cells over the past six decades for their high quality energy output, long life, modularity, reliability and applicability. But fulfilment of cost and efficiency criteria set for its commercialization is still elusive due to high cost and Shockley-Queisser limit (SQ limit) on the efficiency of silicon solar cells, hitherto dominating the solar cell technology. To reduce the processing energy intensity (and hence the cost) and to go beyond the SQ efficiency limit there is a need to look for new PV materials. It makes organic or polymeric material based PV cells a good candidate because of ease of blending of multiple materials and low processing cost. But in spite of the best efforts the efficiency of organic solar cell is still very low as compared to Si solar cells. However the other trade-offs of light weight, large area and flexible shape and form make it very attractive even now. For improvement in the cell characteristics the characteristics of the material employed for the photoactive region, charge separation and collection, and optimization of the device structural components is critical. Due to their unique physical and chemical properties the semiconducting single-walled or
multi-walled carbon nanotubes are attractive candidates for different functions in OPV solar cells.

The single-walled carbon nanotubes not only act as electron acceptor but also as an electrode in organic solar PV cell. The properties of CNT which are useful for solar cells are high carrier mobility, large surface area, enormous current carrying capacity, and tuneable conducting behaviour [33].

Efficiency of a solar PV cell is characterized by its open circuit voltage ($V_{oc}$), short circuit current ($I_{sc}$), and fill-factor (FF). Here $V_{oc}$ of an OPV is dependent on the difference of the molecular energy levels of the dissociated charge carriers while $I_{sc}$ depends on the active area of interface responsible for exciton dissociation. The presence of shunt and series resistances in a solar cell also affect these characteristic parameters. These resistances are determined by the polymeric materials used in the cell design.

As stated earlier the efficiency of organic photovoltaic cell is limited because of low electron mobility, and poor charge separation and transport. It has already been reported that CNTs along with photoactive conjugated polymers bring about drastic changes in the charge transportation and exciton dissociation in organic photovoltaic cell [34-35]. The formation of an interpenetrating blend of polymer as electron donors and carbon nanotubes as electron acceptor can solve some part of these problems. The charge separation in the mixture of donor and acceptor materials is achieved due to a band offset at the interface. The collection of charge carriers in the respective electrode is achieved because of the existence of a bi-continuous network along which electrons and holes can travel through the electron acceptor and the electron donor. The blend can be considered as a network of donor and acceptor heterojunctions that allows efficient exciton dissociation and balanced bipolar transport through its entire volume.

The carbon nanotubes can also be used as an electrode in organic solar cell. There are different criteria for selecting the electrodes in organic solar cell. It is based on the contact between electrode and the active layer (ohmic or not), the energy level alignment, the transparency of the electrode etc. For certain type of solar cells some of these factors are very specific. In bulk heterojunction solar cells the electrode should be carrier selective. The work function difference between two electrodes is not an important factor in organic solar cell. Because, the exciton dissociation is caused by the band-offset at donor – acceptor interface and the exciton binding energy is larger than the internal electric potential drop across the exciton. Currently, the material of choice
as transparent anode in organic photovoltaic cell is (indium tin oxide) ITO and (fluorine doped tin oxide) FTO coated glass.

In 1998 Curan et al. demonstrated the use of multiwalled carbon nanotubes (MWCNT) to increase the conductivity within poly (p-phenylene vinylene) (PPV) [36]. They made a blend of PPV with 15% of CNTs by mass and got improvements of five orders of magnitude of conductivity. The use of MWCNT in the organic photovoltaic cell was first investigated by Ago et al. [37]. They used a layer of CNT as a cathode in PPV/Al diode. The polymer-nanotube composite was prepared by spin coating, using high concentration of MWCNT. The external quantum efficiency of the device was larger than the device having ITO as the electrode. The first SWCNT-conjugated polymer photovoltaic device was reported by Kymakis and Amaratunga in 2002 [38]. They made a blend of P3OT with low SWCNT concentration sandwiched between ITO and Al electrode. The CNT-P3OT interfaces act as dissociation centre for excitons on polymer and electron transport via the nanotubes to the metal electrode. With this arrangement the power conversion efficiency increased in comparison to the undoped polymer film by three orders of magnitude. The device reported by Kymakis and Amaratunga’s [38] showed an open circuit voltage ($V_{oc}$) of 0.75 V, which is larger than the theoretical limit calculated by the metal–insulator–metal (MIM) model. As stated earlier, $V_{oc}$ measured is only very weakly dependent on the work function of the metal. From the analysis of the current–voltage characteristics and electron microscopy imaging of the composite structure, it is proposed that the photovoltaic response of these devices is based on the introduction of internal polymer/nanotube junctions within the polymer matrix, which due to a photoinduced electron transfer from the polymer to the nanotube contribute to enhanced charge separation and collection [39]. But due to bandgap problem the cell cannot absorb whole spectrum in the visible range. So photon losses will occur. Use of organic dye is a good solution to this problem. Because dye has the capability to absorb more light and also help in charge transport. Bhattacharyya and Kymakis [40] reported the photovoltaic properties of blend composite of dye, N-(1-pyrenyl) malenide, functionalized SWNT and conjugate polymer in OPVs. The device was fabricated by spin cast from the solution of composite onto ITO coated glass. Improved performance was achieved by functionalizing the SWNT with dye molecules with $V_{oc}$ as 0.6 – 0.7 V and short circuit current was found to increase by more than an order than SWNT-polymer diode without dye. Length of the CNT is critical in actual device performance, because if the length is greater than the thickness of the active
layer then it may get shorted resulting in decrease in its efficiency. To increase the performance Nakhayama and Asakura [41] used cut-SWCNT(by acid treatment) - polymer composite films. Acid treatment by mixture of H₂SO₄ and HNO₃ cut the long CNT and improved dispersion into polymers as well. The film showed high electrical conductivity depending on the concentration of CNTs. They reported a cell of about three times higher short circuit current than the one not including nanotubes.

**Challenges**

The use of CNT in organic photovoltaic cell leads to solve some of the problems. But there are several other factors in using CNT, because of which the efficiency is limited. Firstly, the mismatch of optical absorption spectra of the polymer and CNT, because of which total absorption of the cell will not match with solar spectrum. Secondly, the wide range of electrical conductivity of CNT depending upon the morphology, the conductivity of CNT ranges from metallic to semiconducting. Thus, each type of CNTs has to be identified for different architectures. Thirdly, at low concentration of CNT the dissociation of exciton is incomplete and at high concentration the dissolving in polymer matrix decreases the efficiency of the cell. Finally, CNT is not soluble in some common solvents.

To overcome the barrier of limited efficiency researchers are trying to incorporate CNTs more efficiently. For efficient exciton dissociation the higher surface area is preferred. Najeeb and Hyeok [42] reported surface modification of CNT to enhance the surface area for efficient exciton dissociation. They purified SWCNT by acidic treatment, carboxylated by chemical oxidation and enhanced improved dispersibility in polymer matrix.

Recently, a new concept of hybrid solar cells with organic and inorganic composites is being studied. Photovoltaic devices based on SWCNT and n-Si heterojunction showed a conversion efficiency of 1.7% [43]. Somani reported a multifunctional device combining the PV action and pressure sensitivity based on n-Si and carbon nanotube using copper pthalocyanine surface modified electrode [44]. Chen and Pan reported a device based on P3HT and Si-MWCNT nanocomposite [45]. The power conversion efficiency of P3HT/Si and MWCNT hybrid film is two to three times better in comparison to simple P3HT/Si nanoparticles or P3HT/MWCNT. The improved performance is because of efficient charge generation by P3HT/Si nanoparticles bulk heterojunction and efficient charge collection.
The use of SWCNT in OPV generates better performance if they are placed vertically aligned. Bissett and Shapter showed better photocurrent response of vertically aligned SWCNT array in visible light [46]. The solubility of nanotubes also plays a major role in the efficiency of the cell. Nie and Guo reported that the water solubility of carbon nanotubes can be increased [47]. They used functionalized CNTs with polyethylene glycol synthesized by a cyclo-addition reaction. Functionalization affords a large increase in aqueous solubility of CNTs.

The use of quantum dot concept also leads to increase the power conversion efficiency of the cell. Shukla and Tymish reported enhanced efficiency by blending of IR sensitive quantum dots and CNTs [48]. The presence of CNTs in QDs shows quenching of the IR photoluminescence. They reported a device with PbSe QD: CNT/P3OT, which shows a better performance than PbSe: P3OT without CNTs.

The use of hybrid nanocomposites like SWCNT and polyaniline (PANI) increases the performance of solar cells. Yao and Chen reported a hybrid nanocomposite containing CNTs and polyaniline for enhanced thermoelectric performance [49]. The SWCNT/PANI nanocomposites show higher electrical conductivity and Seeback co-efficient, which could be attributed to the enhanced carrier mobility in the ordered chain structure of PANI. The present work intends to take this route because of superior properties of hybrid nanocomposites, for OPV application. However demonstration of applicability of CNT prepared from plant based precursors is another challenge. The growing number of scientific publications contributing to OPVs is shown in the Figure 1.3 [50].

1.4.2. Bio-energy and biofuels

Bio-energy is a form of renewable energy derived from biological sources. Biomass is any organic material which stores sunlight in the form of chemical energy. Even though such biofuels are made from plant material and hence are a renewable source, they are not as ‘green’ as they seem. To produce biofuels, large amount of land is need to cultivate the crop, together with irrigation, use of fertilizers, transportation, conversion and refining processes. All these require energy input and emit carbon dioxide. There are a large and growing number of studies that suggest that the use of current biofuels would save very little greenhouse gas, destroy wildlife habitats, as well as affect indigenous and rural poor communities around the world. Biofuels are one of the forms of energy made from biomass. It is used as transport fuel and it may be
produced from a wide range of plant materials (biomass). Biodiesel and bio-ethanol are well known biofuels. Other forms of bio-energy, for example biogas, combustible biomass, generally have a higher overall efficiency. As the world is going to witness a transition between petroleum to renewable very soon, biofuels in general and biodiesel in particular would be the bridge between these. If managed sustainably, biofuel has its merits and is key to tackle global climate change.

Figure 1.3: Number of papers published in scientific journals in the area of OPVs from January 2000 to March 2012 (Search done through ISI, Web of Science)

Biodiesel may be produced by the trans-esterification reaction. The process involves a reaction between a triglyceride and an alcohol to form esters and glycerol. A triglyceride is a glycerin molecule with three long fatty acid chains attached to it. The triglyceride reacts with the alcohol, either methanol or ethanol but most often methanol, in the presence of a catalyst such as sodium hydroxide or potassium hydroxide, to form mono-alkyl ester and crude glycerol. The combination of methanol and potassium hydroxide is preferred in fatty acid methyl ester (FAME) production because biodiesel produced in this way is less resistant to oxidation than typical fossil fuel untreated with additives [51]. The general mechanism of oxidation in biodiesel has been well documented. Fatty acids present in biodiesel, in general, are more susceptible to oxidation because they vary in level of unsaturation, meaning there are more carbon-
carbon double bonds and fewer hydrogen molecules on the fatty acid chains. When biodiesel made from unsaturated oil is exposed to oxygen, the oxygen attaches itself to the bis-allylic site directly adjacent to the two double bonds, which initiates an autoxidation chain reaction sequence. Oxidation stability is not related to the number of double bonds available but rather the number of bis-allylic sites [52]. The initiation step is the formation of a free radical that can react directly with oxygen. This leads to the formation of a peroxide or hydroperoxide molecule. The most reactive site for initial formation is the bis-allylic position. The radicals formed at the bis-allylic sites immediately isomerize to form a more stable conjugated structure, which reacts directly with oxygen to form peroxide. The existence of these molecules is an early indication of oxidation taking place, and it is measured in terms of peroxide value [53]. Later, aldehydes and ketones are formed. Finally, during the polymerization process, resins are produced making the fuel unusable [53]. Thus, the major problem with biodiesel is their susceptibility towards oxidation. The regulations put in place for biodiesel advancement resulted in the rapid development of standardization of specification of the test procedures. These testing specifications all include oxidation stability as a major test method requirement. The trend of scientific publications contributing to Biodiesel storage and their performance in IC engine is shown in the figure 1.4 [54]

Figure 1.4: Number of papers published in scientific journals in the area of biodiesel storage from January 2000 to March 2012 [54]
Challenges

The production of biodiesel were studied by many researchers using various feed stock [55, 56]. But the major setback with biodiesels is their short shelf-life due to rapid oxidation. Karavalakis et al. have studied the stability and aging effect of biodiesel blends with different antioxidants [57]. Antioxidants like butylated hydroxytoluene (BHT), propyl gallate (PG), pyrogallol (PA) and butylated hydroxyanisol (BHA) displayed very low effectiveness in neat biodiesel. Hence, they designed a process to simulate the ageing of an automotive biofuel stored in the fuel tank of a vehicle. The results showed a sharp decrease in fuel stability over time [57]. Similar studies were conducted by Obadiah et al. [58] and Jain and Sharma [59-60] on biodiesels. Tung oil biodiesel characteristics were studied by Shang et al [61]. The results obtained show that B20 or lower blends could meet the specification of ASTM D7467 after storage for a month. Corn biodiesel was also found to be unstable for long hours of storage due to oxidation [62]. Along with natural antioxidants, researchers have also tried synthetic antioxidants to enhance the oxidation stability of the biodiesel. The potency of synthetic antioxidants for biodiesel storage was also studied by Focke et al. [63]. The use of antioxidants could not stop the oxidation completely but could enhance the shelf-life of biodiesels.

Another problem with biodiesel storage technology is related to emission characteristics and engine performance. The antioxidants, that are used, form homogeneous mixture with the biodiesel and it is not economically viable to separate them before they are fed to IC engine. The incorporation of antioxidants in biodiesel has adverse effects on the engine performance [64]. The use of antioxidants (viz. L-ascorbic acid, α tocopherol acetate, butylated hydroxytoluene, p-phenylenediamine and ethylenediamine) on biodiesel were found to control NOx emission, however a substantial increase in unburned hydrocarbon and COx emissions could be seen [65]. Xue et al. have also found that addition of antioxidants affects the engine performance [66]. Thus, the use of existing homogeneous antioxidants poses another set of problems in the form of adverse effects of these antioxidants on engine performance and air pollution. The only route to address this problem is to look for higher performance antioxidants which may be separated out before use.
1.5. Origin of present work and Objectives

As discussed above, the fossil fuel based precursors for CNT synthesis are non-renewable, and the present technology may not sustain without exploring for renewable precursors for the synthesis of CNTs. This not only requires intense search for precursors but also for suitable catalyst and synthesis technique. North-eastern India is known for its floral biodiversity. Thus it calls for search for plant species rich in oil content (in seeds) which may be used for CNT synthesis. The oil extracted from plants may contain various fatty acid component. As discussed, CVD is considered for CNT synthesis because of its low energy intensity process as compared to other techniques. It can be scaled up of mass production as well. Thus, the next steep includes development and/or modification of CVD setup for plant precursors.

The parameters for CNT synthesis from potential precursors needs to be optimized for acceptable quality and higher quantity. Due to existence of large number of parameters influencing these a resort is taken to statistical optimization technique. This would help researchers to synthesize different morphologies of CNTs for different applications.

The two active areas of research in energy technology and systems are solar OPV cells and biodiesel storage. CNT finds applications in these due to its unique characteristics. There are a number of problems in OPV which may be solved appropriately through the CNTs synthesized from plant precursors to get the desired result.

The problems with biodiesel, discussed earlier, suggests for the need of a heterogeneous antioxidant that can be removed before end use.

The present thesis attempts to sort out the above mentioned problems. The main aim of the thesis is to search plant based renewable precursors for CNT synthesis and to utilize the CNTs for application in OPVs and biodiesel storage. However, the specific objectives are:

i. To search and screen renewable plant based precursors for CNT synthesis.

ii. To optimize and evaluate the effect of each of the process parameters for acceptable quality and high quantity.

iii. To suitably utilize the CNTs in OPV architecture and to study its impact on performance.
iv. To investigate and propose a heterogeneous antioxidant based on CNT for biodiesel storage.

1.6. Summary of the thesis

The thesis, consisting of six chapters and two appendices, dwells upon the above mentioned issues in detail as outlined here,

Chapter 1: It introduces the theme of the thesis including information about renewable energy resources in India, potential of solar and biofuels and application of CNTs in these areas. It also describes the need and importance of renewable plant based precursors for CNT synthesis. A detailed literature survey with regard to synthesis and applications of CNTs with a view to provide rationale of the work and to set the objectives are discussed.

Chapter 2: This chapter starts with the details of the process adopted to select plant precursors from different parts of North-east India which is one of the hot spots of the floral species and biomass resources found in the tropical regions of the globe. Few suitable plant varieties were screened for this purpose on the basis of availability, alternative commercial applications and oil content for carbon nanotube synthesis. In the next section of the chapter the synthesis of catalyst, and development & modification of the CVD setup for synthesis of CNT from plant precursors are discussed in detail.

The morphology and yield of CNTs synthesized from each precursor is carefully analyzed to sort them out based on suitability of each one of these for a particular application envisaged in the thesis.

Chapter 3: This chapter is dedicated to refinement of the process of synthesis by optimizing the process parameters like temperature of synthesis, flow rate of carrier gas, catalyst type and precursor type both for improving yield and quality of MWCNT. Taguchi robust technique has been used for the purpose. The six plant precursors, selected earlier, are divided on the basis of major fatty acid content. Three levels of catalyst types, flow rates, and synthesis temperature have used for optimization. The effect of each parameters on the synthesis is also important for acceptable quality and yield of CNTs. This is done to screen out some of them if they did not conform to the requirements. Taguchi robust technique is the best method to evaluate and optimize the process parameters. On the basis of preliminary analysis some of them appeared to be
potential candidates for organic solar cell application, for development of electrodes for fuel cells and to work as a substrate for heterogeneous antioxidants.

**Chapter 4:** The solar photovoltaic cells are developed from inorganic or organic photoactive materials. The technology for inorganic material based PV cells is proven and popular. However, the organic photovoltaic cells have many advantages over inorganic counterpart due to favourable economics, flexibility, form-factor independence and low energy intensity based fabrication technology. The major issue in organic photovoltaic cell is the efficiency and life time. Literature suggests that the use of carbon nanomaterials has improved the efficiency of the organic photovoltaic cells. CNTs have few problems like low dispersibility in organic solvents, the long tubular structure and the high workfunction of MWCNT. Some of these problems are addressed through suitable functionalization of the CNTs. The chapter also describes a method to cut MWCNTs using simple chemical route.

Finally, the chapter describes the application of the modified MWCNTs in OPVs. Three OPV devices, fabricated to understand the effect of pristine, functionalized-cut MWCNTs, have been investigated. The device architecture investigated are - Al/LiF/P3OT+PCBM/ITO (used as baseline device for the study), Al/LiF/P3OT+PCBM+MWCNTs/ITO and Al/LiF/P3OT+PCBM+fc-MWCNTs/ITO and Al/LiF/P3OT+PCBM+fc-MWCNTs/PANI+fcMWCNT/ITO. The device with functionalized-cut MWCNTs showed best performance.

**Chapter 5:** Biodiesel technology has attracted keen interest of the stakeholders in the past decade and is being projected as an alternative future fuel. But, one of the major limitations of biodiesel is its short shelf-life. This is due to the degradation of biodiesel through the process of oxidation. At present homogeneous antioxidants are used to enhance the shelf-life of the oils (both mineral and bio-oil). But these homogeneous antioxidants cannot be removed before use and are consumed during the end-use. Moreover, in the case of biodiesel the engine performance and exhaust emission is affected by the addition of antioxidants. This chapter discusses a new nanomaterial structure which is engineered to contain a magnetic nanoparticle and an antioxidant attached to a substrate. The idea has a potential to make the antioxidant removable without affecting the performance of the engine.

This chapter also dwells upon the basics of biodiesel storage issues and analyzes the results of experiments which were designed to investigate the efficacy of the antioxidant material system.
Chapter 6: This chapter concludes about the synthesis of MWCNTs from plant precursors and their application in organic solar cells and bio-diesel storage. It also discusses about the scope of improvements in OPV and bio-diesel storage systems.

Appendix I : A method to utilize solid waste products like Polypropylene (PP) and Polyethylene terephthalate (PET) for synthesis of MWCNT has been demonstrated.

Appendix II : The utility of MWCNTs (synthesized from plant based renewable precursors) in Alkaline Fuel Cell electrode is discussed.
Reference


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