INTRODUCTION

1.1 LEADING ENERGY CRISIS

Energy supply has arguably become one of the most important problems facing humanity. On an average 30 times more energy is used to make our life more comfortable. Electrical energy is one of the most useful forms of energy, since it can be used for almost everything. As the world is becoming advanced in technology and economy, more energy is being consumed to keep up the development and the demand on energy boomed over the past years. World energy consumption is projected to expand by 50 percent from 2005 to 2030. The Intergovernmental Panel on Climate Change (IPCC) predicts that the global energy need will increase by almost a factor of five over the next century, from 10 TW to near 46 TW by 2100. The IPCC also predicts that burning fossil fuels alone will not be able to meet this requirement and, in order to meet global energy needs, at least 10 TW, will have to be provided from alternative energy sources by 2050 [1]. It wasn't until recent that the severe negative side effects of combusting fossil fuels became evident. Two critical issues have arisen; the effects of by-products of fossil fuel synthesis and combustion and the short supply of the remaining non-renewable fuels. The synthesis and combustion of fossil fuels generates massive amounts of CO₂ which can have detrimental effects on the atmospheric conditions of the earth. The atmosphere itself is already composed of the green-house gases (O₃, H₂O, and CO₂) which help to regulate the incident solar energy and the escaping thermal energy through absorption, reflection, and re-radiation. The excess generation of CO₂ could have profound effects on the surface climate of the earth including global warming, severe
weather pattern shifts and more intense seasonal conditions. On top of this, the amount of fossil fuels left for garnering is dwindling [2-5]. In addition, the burning of fossil fuels releases almost 7 Giga ton of carbon dioxide into the atmosphere each year. Carbon dioxide is a green-house gas and has been linked to global temperature rise through the detailed analysis of CO₂ content in air pockets trapped in ice cores obtained by drilling in Antarctica, Greenland and glaciers. Atmospheric CO₂ has increased by 30% from 280 to 370 ppm by volume since the beginning of the 20th century and the industrial revolution. This increase is thought to be a result of 160 billion tons of CO₂ released into the atmosphere. This is the same increase in CO₂ that naturally occurred starting approximately 110,000 year ago and was partially responsible for a 6 °C temperature increase and the end of the last ice age. Warming of the climate system now is unequivocal, according to many different kinds of evidence. Observations show increases in globally averaged air and ocean temperatures, as well as widespread melting of snow and ice and rising globally averaged sea level. One of the predicted consequences of anthropogenic CO₂ increase is an average global temperature rise of almost 6 °C by 2100. Such a dramatic rise would cause thermal expansion of the oceans as well as melting of polar ice caps, resulting in floods and storms that would contaminate drinking water and cause a very serious global health and safety crisis. The energy crisis facing humankind has the potential for disastrous consequences and solutions need to be pursued with a great sense of urgency. In order to combat this impending energy crisis, and the catastrophic consequences of global warming, carbon-free alternative energy sources will need to be used to meet the ever increasing global energy demand. The United States Department of Energy is considering a variety of
alternative energy sources as a potential solution to the energy problems. The increasing energy demand will probably be met with a combination of bio-energy, nuclear energy, hydroelectric power, hydrogen, solar power, geothermal power, natural gas and wind power [6-8]. Due to the exponential increase of population and economic rise of many un-developed countries, the world energy consumption is going parallel. In 2010 the total world energy consumption was up to 15 TW and in 2012 it had risen to 16 TW. It is projected that by 2050 the worldly power consumption will rise up over 26 TW. Figure 1 shows the percentage consumption of various energy sources. Plot shows that non-renewable sources (nuclear and fossil fuels – oil, coal and natural gas) constitute well over 90% of the total energy consumed with less than 10% coming from the renewable sources. Among the renewable sources, solar and wind show the most potential energy sources [9-10].

![Pie chart showing energy consumption percentages](image)
1.2 ALTERNATIVES TO PRESENT ENERGY ECONOMY

The sun deposits $4.3 \times 10^{20}$ J of energy onto the earth in one hour, which is more energy than mankind consumes in one year. Of the 174 PW that reaches the earth’s outer atmosphere, 86 PW still reaches the earth’s surface; the other 88 PW being absorbed or reflected by the atmosphere. Using a combination of the renewable sources would provide more than enough energy for sustainability but solar alone could also accomplish this. If only 0.16% of the earth’s surface was covered with solar energy conversion systems that were at least 10% efficient, the energy requirements would be satisfied [11-12].

1.3 PHOTOVOLTAICS

Photovoltaic (PV) is a method of generating electrical power by converting solar radiations into direct current electricity using semiconductors at the junction of two substances that exhibit the photovoltaic effect. Direct harvesting of solar energy to electricity is called “photovoltaics”. Photovoltaic generation employs solar panels composed of a number of solar cells containing a photovoltaic material. Materials presently used for photovoltaics include monocrystalline silicon, polycrystalline silicon. The life on the ground has been always governed by solar power. As early as in the 7th century B.C., magnifying glass was already used to concentrate sun’s rays to make fire. Later on, the Roman people built the famous bath-houses (in the fourth century A.D.) with large south facing windows to employ the sun’s warmth. They named these sun-spaces as *heliocamini* (sun furnaces) before the discovery of photovoltaic effect [13]. In 1839, Edmund Becquerel, a French experimental physicist of nineteen years old, noticed the generation of an electric current while experimenting with a silver coated platinum
electrode placed in the electrolyte. Since this discovery many effort have been made in this field. In 1883, an American inventor [14] developed the first large area solar cells from selenium wafers. However, since the selenium cells converted far less than 1% of all incident sunlight into electric power and deteriorated very rapidly when exposed to strong light, these pioneers in photoelectricity failed to build the solar devices that they had hoped to. These preliminary results opened the doors in this technology, which is nowadays amongst hot research topics. The spectral distribution of the solar spectrum was described by Max Planck in 1901 through his Planck's law [15]. Four years later, Albert Einstein published a simple description of “light quanta” (later called “photons” as suggested by Gilbert Lewis in 1926) and showed how they could be used to explain the photoelectric effect [16]. This is the theoretical basis for all photovoltaic devices and in common semiconductors, photons excite electrons out of the valence band and into the higher-energy conduction band, where they are collected and transported to the outer circuit. In 1904, Wilhelm Hallwachs made a semiconductor-junction solar cell from copper and copper oxide, a prototype of thin-film Schottky barrier device. This barrier layer at the semiconductor-metal interface was confirmed by Goldmann and Brodsky in 1914 [17] and later studied in more detail by Walter Schottky, Neville Mott and others [18, 19]. In 1932, Audubert and Stora discovered the photovoltaic effect in cadmium sulfide (CdS), opening up a way to IIb - VIa group elements for solar cells [20]. In the 1950s with the development of silicon electronic, Fuller [21], intuitively made near-surface p-n junctions by boron trichloride treatment of n-type silicon wafer which greatly favoured charge separation of the device. With these substrates, Chapin had got near 6% conversion efficiency which was 50 times more efficient than the selenium cells [22].
After this findings, many kinds of $p$-$n$ junction with CdS, GaAs, InP and CdTe were developed, however the cost of the photoelectricity was so high (several hundred $ per Watt) and was exclusively used in space application. In the 1970s after the work of Dr. Berman’s, the cost of single crystal module is cut down to 10-20 $ per Watt [23]. In the mid 1970s, after the political crisis in the Middle East, the restriction and the realization of the limitations in fossil fuel resources, a great interest in the solar cell as an alternative energy source for terrestrial application, awoke. It was during this period that second generation solar cells were developed, such as polycrystalline and amorphous silicon, thin-film deposits of silicon, CdTe, CuInSe$_2$, (CIS) and Cu(In,Ga)Se$_2$ (CIGS), as well as multijunction cell technology. This generation of device turned out to be advantageous in production cost with respect to silicon device [24].

1.4 HISTORY OF NANOPARTICLES

Nanoparticles themselves had been around and studied long before the words were coined. For example many of the beautiful colors of stained glass windows are a result of the presence of small metal oxide clusters in the glass, having size comparable to the wavelength of light. Particles of different size scatter different colors. Small colloidal particles of silver are a part of the process of image formation in photography.

The current widespread interest in nanotechnology dates back to the year 1996 to 1998 when a panel under the auspices of the world technology evaluation center (WTEC), funded by the national science foundation and other federal agencies undertook a worldwide study of research and development in the area of nanotechnology.
Richard Feynman in 1960 presented a visionary and prophetic lecture at a meeting of the American Physical society entitled "There is plenty of room at the bottom" where he considered on the possibility and potential use of nanosized materials. A magnetic fluid called ferrofluids were developed in 1960's they consists of nanosized magnetic particles dispersed in liquids. Structural features of metal nanoparticles such as the existence of magic numbers were revealed in the 1970's using mass spectroscopic studies of sodium metal beams. Groups at Bell laboratories and IBM fabricated the first two dimensional quantum wells in the early 1970's. They were made by thin -film (epitaxial) growth technique that build a semiconductor layer one atom at a time. That leads to the development of zero dimensional quantum dots, which is now one of the more matured nanotechnologies commercial applications.

In 1981, a method was developed to make metal clusters using a high powered, focused laser to vaporize metals into hot plasma. A gust of helium cools the vapor, condensing the metal atoms into clusters of various sizes. In 1985, this method was used to synthesize fullerene (C_{60}). The first three dimensional periodic photonic crystal possessing a complete band gap was fabricated by Yablonovitch in 1991. In the 1990's lijima made carbon nanotubes, and super conductivity and ferromagnetism were found in C_{60} structures.

If only one length of a three dimensional nanostructure is of a nanometer dimension, the structure is known as a quantum well and the electronic structure is quite different from the arrangement where two sides are of nanometer length, constituting what is referred to as quantum wire. A quantum dot has all three
dimensions in the nanometer range. The changes in electronic properties with size result in the optical properties of nanosized materials.

1.5 NANOSCIENCE

The prefix \textit{nano} in the word nanomaterials means a billionth \((1 \times 10^{-9})\). If the material size is of the order of a billionth of a meter, at least in one dimension, then it is termed as a nano structured material or a nanomaterial. The existence of functional devices and structures of nanometer dimensions is not new. For example, in fourth-century A.D. Roman glass makers were fabricating glasses containing nanometer size metals. Artifacts from this period, the Lycurgus cups, which contain metal nanoparticles reside in the British Museum in London. Medicinal preparation called Jasada Bhasma is being used in the traditional Ayurvedic system of healing using metals, germs and herbs that originated in India even before 800 A.D. [25]. However, a systematic study of these structures for potential application is relatively new. Nanomaterials have the potential to be applied in different fields such as bio-sensors [26], catalysis [27], light emitting devices [28], quantum devices [29, 30], dye-sensitized solar cells etc. Nanostructured materials have large surface to volume ratio compared to their bulk counterparts. In addition, the de-Broglie wavelength of charge carriers is comparable to the physical size of the nanomaterials. So the materials start showing quantum mechanical phenomenon when size of bulk material reduces to nanometer range. It is referred to as the quantum size effect (QSE). In this nanometer range, the physical properties become very sensitive to the shape and size of the material. To illustrate this fact, the theoretical understanding on how energy states for conduction electrons and their distribution is related to shape and size of the material is briefly given below.
In a bulk material, carriers are free to move in all three dimensions and hence, the material is termed as a three dimensional (3D) system. If one of the spatial dimensions of the material is in nanometer range, while the other two remain larger than the resulting structure is called as quantum well. Quantum well is termed as a two-dimensional (2D) system since carriers are free to move in two dimensions and confined in one dimension. If two spatial dimensions of a material are in nanometer range but the other one is larger, then the resulting structure is called quantum wire. Quantum wire is considered to be a one-dimensional (1D) system. Here the carriers are confined in two dimensions but free to move in one dimension. If all the three dimensions of a material are in nanometer range then the resulting structure is called as quantum dot. Quantum dot is considered to be a zero-dimensional (0D) system since carriers are confined in all the three dimensions. In zero dimensional systems, energy levels are entirely discrete [31-36].

Materials in nano size range exhibit some remarkable specific properties; a transition from atoms or molecules to bulk form takes place in this size range. For example, crystals in the nanometer scale have a low melting point (the difference can be as large as 1000 °C) and reduced lattice constants, since the number of surface
atoms or ions becomes a significant fraction of the total number of atoms or ions and the surface energy plays a significant role in the thermal stability. In general, nanotechnology can be understood as a technology of design, fabrication and applications of nanostructures and nanomaterials. Nanotechnology also includes fundamental understanding of physical properties and phenomena of nanomaterials and nanostructures. Study on fundamental relationships between physical properties and phenomena and material dimensions in the nanometer scale, is also referred to as nanoscience. There are various reasons why nanoscience and nanotechnologies are so promising in materials, engineering and related sciences. What makes nanotechnologies really interesting to scientists and companies? First thing is types of properties that often change at nano scale: optical (e.g. colour, transparency), electrical (e.g. conductivity), physical (e.g. hardness, melting point), chemical (e.g. reactivity, reaction rates). Nanotechnology is not simply working at ever smaller dimensions; rather, working at the nano scale enables scientists to utilize the unique physical, chemical, mechanical and optical properties of materials that naturally occur at that scale. This is a consequence of the small size of nanomaterials, physically explained as quantum effects. The consequence is that a material (e.g., a metal) when in a nanosized form can assumes properties which are very different from those when the same material is in a bulk form. For instance, bulk silver is non-toxic, whereas silver nanoparticles are capable of killing viruses upon contact. Nanosized gold appears red in colour. The particles are so small that electrons are not free to move about as in bulk gold (bulk gold appears yellow colour). Because electron movement is restricted,
the particles react differently with light. Properties like electrical conductivity, colour, strength and weight will be changed at the nanoscale level [37, 38].

1.6 NANOTECHNOLOGY

The progress of technology and quality of life of mankind has always been close knit with the progress in material science and material processing technology. Recent developments in nanotechnology and demonstrations of various quantum size effects in nano scale particles, implies that most of the novel devices of future will be based on properties of nanoparticles.

Nanoscience and nanotechnology is a highly multidisciplinary field of applied science and technology covering a broad range of topics. The main unifying theme is the control of matter on a scale smaller than 1 micrometer, normally between 1-100 nanometers, as well as the fabrication of devices on this same length scale. At this length scale, nanomaterials have very large surface to volume ratio, and quantum confinement starts to play an important role. The increase in the surface area to volume ratio which is a gradual progression as the particle gets smaller, leads to an increase in dominance of the behavior of atoms on the surface of a particle over that of these in the interior of the particle. As a result, nanomaterials are found to possess unique or enhanced properties compared with their bulk counterparts and more and more devices, such as electrodes, fuel cells, carbon nanotubes etc are to be fabricated to utilize these properties [39].

Nanomaterials can be classified into zero-dimensional, one-dimensional, and two-dimensional nanomaterials. Being confined in all three dimensions, quantum dots are obtained. Crystals in the nanomaterials scale have a low melting point and reduced
lattice constants and these are stable at much low temperature. So ferroelectrics and ferromagnetics may lose their ferro electricity and ferromagnetism when the materials are shrunk to the nanometer scale. Bulk semiconductors become insulators when the characteristics dimension is sufficiently small.

New behavior at the nanoscale is not necessarily predictable from that observed at large size scales. The most important changes in behavior are caused not by the order of magnitude size reduction, but by newly observed phenomena intrinsic to or becoming predominant at the nanoscale, such as size confinement, predominance of interfacial phenomena and quantum mechanics [40]. Once it is possible to control feature size, it is also possible to enhance material properties and device functions beyond those that we currently know or even consider as feasible. Reducing the dimensions of structures leads to entities, such as carbon nanotubes, quantum wires and dots, thin films, DNA-based structures, and laser emitters, which have unique properties. Such new forms of materials and devices herald a revolutionary age for science and technology, provided we can discover and fully utilize the underlying principles.

Developments during the past decade in biochemistry, physical chemistry, microscopy and engineering have resulted in a tremendous upsurge of interest in the properties of very small particles and their possible applications in a wide variety of products. Materials dispersed in nanometer size generally show very dissimilar properties compared to their appearance in large measurement. Transition from microparticles to nanoparticles can lead to a number of changes in physical properties. Two major factors in this are the increase in the ratio of
surface area to volume, and the size of the particle moving into realm where quantum effects predominate. This irregular behavior assures their application under unusual conditions. Intensive research effort has been spent on the preparation, characterization and application of nanostructures [41].

1.7 CHALLENGES IN NANOTECHNOLOGY

Challenges include the building and demonstration of novel tools to study at the nanometer level what is being manifested at the macro level. The small size and complexity of nanoscale structures make the development of new measurement technologies more challenging than ever. New measurement techniques need to be developed at the nanometer scale and may require new innovations in metrological technology. Measurements of physical properties of nanomaterials require extremely sensitive instrumentation, while the noise level must be kept very low. Although material properties such as electrical conductivity, dielectric constant, tensile strength, are independent of dimensions and weight of the material in question, in practice, system properties are measured experimentally. For example, electrical conductance, capacitance and tensile stress are measured and used to calculate electrical conductivity, dielectric constant and tensile strength. As the dimensions of materials shrink from centimeter or millimeter scale to nanometer scale, the system properties would change accordingly, and mostly decrease with the reducing dimensions of the sample materials. Such a decrease can easily be as much as 6 orders of magnitude as sample size reduces from centimeter to nanometer scale.
For the fabrication and processing of nanomaterials and nanostructures, the following challenges must be met:

- Overcome the huge surface energy, a result of enormous surface area or large surface to volume ratio.
- Ensure all nanomaterials with desired size, uniform size distribution, morphology, crystallinity, chemical composition, and microstructure, that altogether result in desired physical properties.
- Prevent nanomaterials and nanostructures from coarsening through either Ostwald ripening or agglomeration as time evolves [42].

1.8 APPLICATIONS OF NANOMATERIALS

Small amounts of nanoparticles are producing significant property improvements in applications to be found across all industries, particularly aerospace, automotive, electronics, medical, glass, optics and consumer goods. The potential benefits of nanotechnology are pervasive, as illustrated in the fields outlined below:

1. Materials and Manufacturing

Nanotechnology is changing the way of materials and devices that will be produced in the future. The ability to synthesize nanoscale building blocks with precisely controlled size and composition and then to assemble those into larger structures with unique properties and functions will revolutionize segments of the materials manufacturing industry. Application include (a) manufacturing of nanostructured metals, ceramics and polymers at exact shapes without machining; (b) improved printing brought about by nanometer-scale particles that have the best properties of both dyes and pigments; (c) nanoscale cemented and plated carbides and nanocoatings for cutting tools, electronic,
chemical, and structural applications; (d) new standards for measurements at nanoscale, and (e) nanofabrication on a chip with high levels of complexity and functionality.

2. Nanoelectronics and Computer Technology

Potential breakthroughs include (a) nanostructured microprocessor devices that continue the trend in lower energy use and cost per gate, thereby improving the efficacy of computers by a factor of millions; (b) communication systems with higher transmission frequencies and more efficient utilization of the optical spectrum to provide at least ten times more bandwidth, with consequences in business, education, entertainment, and defense; (c) small mass storage devices with capacities at multi-terabit levels, a thousand times better than today; and (d) integrated nanosensor systems capable of collecting, processing, and communicating massive amounts of data with minimal size, weight, and power consumption. Potential applications of nanoelectronics also include affordable virtual reality stations that provide individualized teaching aids (and entertainment); computational capability sufficient to enable unmanned combat and civilian vehicles; and communication capability that obviates much commuting and other business travel in an era of increasingly expensive transport fuels.

3. Medicine and Health

Artificial inorganic and organic nanoscale materials can be introduced into cells to play roles in diagnostics (e.g., quantum dots in visualization), but also potentially as active components. Finally, nanotechnology-enabled increases in computational power will permit the characterization of macromolecular networks in realistic environments. Such simulations will be essential in developing biocompatible
implants and in the drug discovery process. Potential applications include (a) rapid and more efficient genome sequencing enabling a revolution in diagnostics and therapeutics; (b) effective and less expensive health care using remote and invivo devices; (c) new formulations and routes for drug delivery that enormously broaden their therapeutic potential by targeting the delivery of new types of medicine to previously inaccessible sites in the body; (d) more durable rejection-resistant artificial tissues and organs; (e) enable vision and hearing aids; and (f) sensor systems that detect emerging disease in the body, which will ultimately shift the focus of patient care from disease treatment to early detection and prevention.

4. Aeronautics and Space Exploration

Nanostructuring is also critical to design and manufacture of lightweight, high strength, thermally stable materials for planes, rockets, space stations, and planetary/solar exploratory platforms. Moreover, the low-gravity, high-vacuum space environment may aid the development of nanostructure and nanoscale systems that cannot be created on earth. Applications include (a) low-power, radiation-tolerant, high performance computers; (b) nano-instrumentation for microspacecraft; (c) avionics made possible by nanostructured sensors and nanoelectronics; and (d) thermal barrier and wear-resistant nanostructured coatings.

5. Biotechnology and Agriculture

The molecular building blocks of life - proteins, nucleic acids, lipids, carbohydrates and their non-biological mimics - are examples of materials that possess unique properties determined by their size, folding and patterns at the nanoscale.
Biosynthesis and bioprocess offer fundamentally new ways to manufacture new chemicals and pharmaceutical products. Integration of biological building blocks into synthetic materials and devices will allow combining biological functions with otherwise desirable materials properties. Imitation of biological systems provides a major area of research in several disciplines.

6. National Security

The Department of defense recognized the importance of nanostructures over a decade ago and has played a significant role in nurturing the field. Critical defense applications include (a) continued information dominance through advanced nanoelectronics, identified as an important capability for the military; (b) more sophisticated virtual reality systems based on nanostructured electronics that enable more affordable, effective training; (c) increased use of enhanced automation and robotics to offset reductions in military manpower, reduce risks to troops, and improve vehicle performance; for example, several thousand pounds could be stripped from a pilot less fighter aircraft, resulting in longer missions, and fighter agility could be dramatically improved without the necessity to limit g-forces on the pilot, thus increasing combat effectiveness; (d) achievement of the higher performance (lighter weight, higher strength) needed in military platforms while simultaneously providing diminished failure rates and lower life-cycle costs; (e) badly needed improvements in chemical/biological/nuclear sensing and in casualty care; (f) design improvements of systems used for nuclear non-proliferation monitoring and management; and (g) combined nano and micromechanical devices for control of nuclear defense systems.
Introduction

Chapter-1

7. Environment

Environmental engineering evolved from an interdisciplinary approach to solving water quality problems that traces its origins to the latter part of the 19th century. The concept of bringing microbiologists, stream ecologists, traditional civil engineers, and aquatic chemists together to resolve problems with dissolved oxygen in surface water originating from waste discharges was revolutionary in its time. This interdisciplinary model for what was first called sanitary engineering was expanded during the last century to include the study of impacts of human activities on air, soils, groundwater, and other environmental media. Today, the standard model for teaching and research in an environmental engineering program covers bases in the areas of air, water, and soil with crosscutting areas of expertise such as fluid mechanics, chemistry, microbiology, physical chemical processes, and, occasionally, policy. Some programs additionally also include a consideration of impacts on human health and ecosystems.

The products of nanochemistry are being used to create new generations of technologies for curing environmental maladies and protecting public health. Water pollution control, groundwater remediation, potable water treatment, and air quality control are being advanced through nanomaterial-based membrane technologies, adsorbents, and catalysts. In water treatment they can be used for a wide spectrum of applications, ranging from particle removal to organic removal and desalination. Membranes are also at the heart of fuel cell technologies. They can be viewed as vehicles for both electricity generation and water fabrication. Nanoscale control of membrane architecture may yield membranes of greater selectivity and lower cost in both water treatment and water fabrication. The replacement of carbon black in tires by
nanometer-scale particles of inorganic clays and polymers is a new technology that is leading to the production of environmental-friendly, wear-resistant tires. Potential future breakthroughs also include the use of nanorobotics and intelligent systems for environmental and nuclear waste management, use of nanofilters to separate isotopes in nuclear fuel processing of nanofluids for increased cooling efficiency of nuclear reactors, of nanopowders for decontamination, and of computer simulation at nanoscale for nuclear safety. Nano crystalline metal oxides are highly effective adsorbents towards a broad range of environmental contaminants ranging from acids, chlorinated hydrocarbons, organo phosphorus and organo sulfur compounds to chemical warfare agents. These materials do not merely adsorb, but actually destroy many chemical hazards by converting them to much safer by products under a broad range of temperatures. Metal oxides produced by nano scale were proven to be no more toxic than their non-nano commercial counterparts and continue to be a great choice for a bating environmental pollutants.

8. Science and Education

The science, engineering, and technology of nanostructures will require and enable advances in many disciplines: physics, chemistry, biology, materials, mathematics and engineering. In their evolution as disciplines, each area is now strengthened and simultaneously equipped to address nanostructures providing a fortuitous opportunity to revitalize their interconnections. The dynamics of interdisciplinary nanostructures effort will reinforce educational connections among disciplines and give birth to new fields that are only envisioned at this moment. Further development of the field requires changes in the laboratory and human resource
infrastructure in universities and in the education of nanotechnology professionals, especially for industrial careers [43, 44].

1.9 HISTORY OF SOLAR CELLS

Solar energy harvesting is an expensive process, because the most promising and efficient devices are constructed from extremely pure materials. The most commonly available, efficient solar cells are based on single crystal silicon. Silicon is very abundant, making up 25.7 percent of the earth’s crust by mass. Even though the element silicon is very abundant, a significant amount of refining is required for solar cell grade silicon. For silicon to be effectively used in solar cells, it needs to be extremely pure to parts per billion. To produce monocrystalline silicon, raw silicon must be refined to metallurgical grade silicon, then refined to semiconductor grade silicon, and further refined by the Czochralski process, creating a large single crystal of silicon. Each process requires the silicon be heated to between 1000 °C and 1900 °C, depending on the process. Finally, once the silicon ingots are made they are cut into wafers and polished which destroys approximately 50% of the silicon. All these processes increase the cost of silicon solar cells. Multi-junction solar cells can cost up to eight times as much as silicon solar cells. High cost associated with multi-junction solar cells is due to the use of rare and hard to process materials, such as gallium, indium and germanium. They suffer from the same expensive processing as do silicon solar cells and the materials are not as abundant, which greatly increases the cost of multi-junction solar cells. In order to make solar energy more economically viable, efficient alternatives must be investigated [45-52]. The best commercial solar cells based on single-crystal silicon are about 18% efficient [53-56]. These conventional p-n junction cells, so-called first-generation devices, suffer from
the high cost of manufacturing and installation. The second-generation devices consisting of CuInGaSe₂ (CIGS) polycrystalline semiconductor thin films can reduce the price significantly, but it does not reduce the challenge to make their efficiencies more practical. Now the third-generation solar cells, such as dye-sensitized solar cells (DSSCs) [57, 58], bulk heterojunction cells [59-61], and organic cells [62] are promising photovoltaic cells for inexpensive and large-scale solar energy conversion. A promising alternative to silicon and multijunction solar cells are dye sensitized solar cells [63-65].

1.10 HISTORY OF DYE-SENSITIZED SOLAR CELLS

Sensitisation of wide band gap semiconductors using dyes has a long history, dating back to early days of photography of the 19th century. Moser observed that the photoelectric effect on silver plates was enhanced in the presence of erythrosine dye [66] and confirmed by Rigollot in 1893 [67]. Systematic mechanistic studies started only in the late 1960's with the work of dye-sensitisation process on ZnO [68-70] and SnO₂ [71-73] electrodes carried out by Gerischer and Memming. Most of these early studies were fundamental in nature, aimed to understand electron-transfer processes involving valence and conduction bands of a semiconductor immersed in a redox electrolyte. Gerischer combined the stability of large band gap semiconductors with the photosensitivity to light in the visible region by dye adsorption onto semiconductor surface. Though, these works were still on their preliminary stage, the dye sensitized cells obtained were characterized with poor dye anchorage (mostly physisorbed) on the semiconductor surface and low conversion efficiencies restricted by the limited, weak light absorption of the dye monolayer on the planar surface. Incremental improvements were then achieved both in the chemisorption of sensitizers [74-76], electrolyte redox chemistry and the judicious
selection of photoelectrode materials [77-83]. Most semiconductors such as CdS, CdSe, GaP and Si underwent serious photocorrosion or even normal corrosion in the dark. Thus a stable and wide band-gap semiconductor, TiO$_2$, became the material of choice. The breakthrough of dye-sensitized devices as solar cell was then achieved with the use of TiO$_2$ having a mesoporous structures with high surface area, which allowed a drastic enhancement of the amount of adsorbed dye. Furthermore the development of metal organic sensitizers and the later panchromatic “black dye” bearing attachment groups which allow the chemical bonding of the sensitizer to the surface of the TiO$_2$ lead to a drastic improvement in charge injection efficiency. Based on these innovations overall efficiencies of over 10% were obtained for dye-sensitised mesoporous TiO$_2$ electrodes in contact with an electrolyte containing an iodide based redox system for dye regeneration [84-88]. A variety of dyes are used in the third generation photovoltaic technology, especially metal free dyes exhibiting high extinction coefficients. Since metal organic sensitizer performed well with a thick TiO$_2$ film, which increases the cell resistance and reduces the photovoltage, metal-free dye with high extinction coefficient could overcome this problem [89-91].

In 1991 Michael Grätzel and Brian O'Regan invented “Dye-sensitized solar cells”, also called “Grätzel cells”. Dye-sensitized solar cells (DSSCs) have been the focus of many investigations worldwide. Since the historic paper on dye-sensitized solar cells (DSSCs) published in 1991 by Prof. M. Grätzel, DSSCs have quickly attracted great attention towards the fabrication of efficient and low-cost solar energy harvesting devices [92-94].
A Dye sensitized solar cells is a relatively new kind of low-cost solar cell that shows great promise because of its low-cost materials and simplicity. DSSC functions because of the interactions between the cells anode and cathode and the TiO$_2$ nanoparticles, which are coated with a light sensitive dye and surrounded by an electrolyte. The anode is transparent like glass, so that sunlight can absorbed by the inner parts of the solar cells. Between the anode and the cathode is a mesh of TiO$_2$ nanoparticles that act like a roadway for the electrons passing through the cell. The TiO$_2$ nanoparticles are coated with light absorbing dye that converts photons (light) into electrons (electricity). An
electrolyte (usually iodide) fills the spaces between the TiO₂ nanoparticles and helps transfer of electrons from the cathode to the dye molecules (after releasing an electron from dye, it needs another to replace the one it lost). On the other end of the cell is the cathode, typically a film of graphite or platinum. The anode sends electrons from the solar cells through a wire to whatever the cell is powering: then the electrons loop back to the cathode. The electrons originate from the dye molecules coating on the TiO₂ nanoparticles when they are hit by light (photons). Different colour dyes can absorb different wavelengths of light, which in turn carry different amount of energy. In reality, the dye nanoparticles are covered all over except where the nanoparticles are connected to other nanoparticles. When the photon strikes a dye molecule, the energy from the photon is absorbed into the dye molecule. The dye molecule enters an excited state and emits an electron. The emitted electron travels the TiO₂ nanoparticles until it reaches the anode. Because the dye molecule just emitted one of its own electrons it will start to decompose unless it receives another electron to replace the one it lost. In this state the dye molecule cannot emit any more electrons. The electrolyte present in between two electrodes contain (I⁻/I₃⁻) ions. The triiodide recovers its missing electrons from the cathode, which reduces triiodide back to three iodide molecules. When all these process work together, an electric current is generated. The electrons emitted from the dye flow from the anode to whatever is powered by the DSSC and then flow into the all through the cathode. Then the electron from cathode restores the electrons needed by the iodide ion in electrolyte, which restores the electrons needed by the dye molecules and the whole process starts over again [95-102].
1.12 APPLICATION OF NANOMATERIALS FOR SOLAR ENERGY HARVESTING

Use of renewable energy is an extremely promising option for both reducing greenhouse gas emissions and enhancing diversity of energy supplies. Unlike nuclear energy or coal-derived fuel, solar-derived energy has no massive scale waste product requiring expensive and environmentally challenging disposal. Environmentally driven carbon taxes that favored renewable energy might be one policy route that would propel the use of solar technologies. But so far, many countries have favored direct subsidies to investors in renewable energy and imposition of renewable energy target standards.

Semiconductor nanowires represent an important class of nanostructure building block for photovoltaics as well as direct solar-to-fuel application because of their high surface area, tunable band gap and efficient charge transport and collection. Many metal oxide semiconductors are stable in chemically aggressive environments, particularly in oxidative environments such as the atmosphere and aqueous media, which affords them long-term stability. Furthermore, metal-oxides such as TiO₂ and Fe₂O₃ are produced in quantities of millions of tons per year. These materials are used in a variety of applications where low cost is critical due to the volume of material required, such as for house paint and building glass. Thus, it is desirable to use these low-cost, industrially-relevant materials for widespread solar energy harvesting. The ability to create high-efficiency solar cells is a key strategy to meeting growing world energy needs. Nanotechnology is currently enabling the production of high-efficiency organic photovoltaics (OPVs) to help meet this challenge. Organic photovoltaics are
nanostructured thin films composed of layers of semiconducting materials and dye that absorb photons from the solar spectrum [103].

1.13 SEMICONDUCTORS

Semiconductors are the materials whose electrical resistivity lies between $10^{-2}$ to $10^9 \, \Omega \, \text{cm}$ at room temperature. The band gap of these materials falls between 0 to 4 eV and this group of materials show many commonality in their physical properties. Semiconductors have attracted considerable attention particularly after the discovery of transistors in 1947 and are the most important materials for fabrication of electronic and optoelectronic devices today. A special note should be made about the distinction between semiconductors and insulators, particularly when applied to metal oxides (MOs). Some MOs are insulators while others are considered as semiconductors, depending on their band gaps. There is no clear-cut consideration about what the band gap energy should be in distinguishing semiconductors and insulators, even though 3.5–4.0 eV is usually chosen somewhat arbitrarily as the dividing point [104]. Materials with band gap larger than this number are often considered as insulators while those smaller are semiconductors. Sometimes, a given metal oxide with a fixed band gap can be considered as insulator or semiconductor, depending on the relevant context. Also, the band gap energy could differ depending on if it is defined optically or electrically. For example, TiO$_2$ and ZnO are considered as insulators optically in most contexts due to weak or no visible absorption. However, they are often considered as wide band gap semiconductors also because of their electrically semiconducting properties usually caused by doping. As a result, semiconductor nanomaterials have attracted significant attention in research and applications in areas including energy conversion, sensing, electronics, photonics and
biomedicine. Parameters such as size, shape and surface characteristics can be varied to control their properties for different applications of interest [105, 106]. Semiconducting nanomaterials possess unique optical and electronic properties including tunable optical absorption due to quantum confinement effects ideally suited for solar energy harvesting applications. The above-band gap light excitation and photogenerated charge carriers (PCCs) can be collected as electricity in photovoltaic solar cells, used directly in photocatalytic redox reactions, or utilized to drive chemical reactions in photoelectrochemical (PEC) devices. Inherent electron hole recombination and charge carrier trapping usually compete with and limit the efficiency of charge separation, collection, transport, or reaction. The advantage of using semiconductor nanomaterials for solar devices is the ability to manipulate their electronic band structures and thereby alter their opto-electronic properties and functionalities. To understand the fundamental charge carrier dynamics, various time-resolved techniques that directly probe the carrier lifetime and behavior have been employed. Some review focuses on new strategies to increase the separation of charge carriers using methods such as quantum dot (QD)-sensitization of metal oxides (MOs), elemental doping or combined approaches for achieving synergistic effects [107]. These devices will revolutionize solar energy harvesting, because they can be manufactured using many methods.

1.14 SYNTHESIS OF NANO SEMICONDUCTORS

Material Scientists are conducting research to develop novel materials with better properties, more functionality and lower cost than the existing ones. Several physical, chemical and biological synthesis methods have been developed to enhance the performance of nanomaterials displaying improved properties with the aim to have a
better control over the particles size, distribution, morphology, purity, quantity and quality, by employing environmental friendly economical processes has always been a challenge for the researchers.

Just as a wall may be built up by piling bricks one over the other, particles may be created by assembling together their building blocks which may be atoms or molecules. This can be done much more easily than trying to break down large particles into nanoparticles. Nanoparticles are synthesized by bringing together atoms or molecules which are initially apart to form a larger cluster of atoms. This is similar to how crystals grow in a solution. However, things are not that simple and these particles quickly grow to be too large. It is thus important to arrest or limit the growth of these particles when they have grown to the desired size.

Nanosemiconductors synthesis requires new synthetic methods to reveal and exploit the complex nature of the nanoscale and to manipulate atoms and molecules into nanostructures. There is a wide variety of techniques for producing nanoparticles such as

A. Plasma arcing
B. Chemical vapor deposition
C. Electrodeposition
D. Sol-gel synthesis
E. Ball milling
F. Microwave technique
G. Co-precipitation
H. Hydrothermal process
A. Plasma arcing

Plasma arcing device consists of two electrodes. Plasma (Ionized gas) is achieved by making gas conduct electricity by providing potential difference across the two electrodes so that the gas phase yields up its electrons and thus ionizes. High current spark across the electrodes produced by breakdown of flowing inert gas vaporizes a small amount of the electrode metals. The voltage required for this process is 10 to 100 V and electric current density is 10-1000 A/cm². Plasma arcing can be used to make deposits on surfaces rather than new structures [108].

B. Chemical vapor deposition

This method involves depositing nanoparticle material from the gas phase. Material is heated to form a gas and then allowed to deposit as a solid on a surface usually under vacuum. There may be a direct deposition or deposition by chemical reaction to form a new product such as nano powders of oxides and carbides of metals. In this method pure metal powders can be achieved by using microwave which is tuned to metal excitation frequencies so that metal melt and vaporizes to produce plasma at a temperature up to 1500 °C. The vapourated plasma is coated on a surface in the form of layers [109, 110].

C. Electrodeposition

Electrodeposition is a special electrolysis resulting in the deposition of solid material on an electrode. This process involves oriented diffusion of charged growth species through a solution when an external electric field is applied. Electodeposition is only applicable to electrical conducting materials such as metals, alloys, semiconductors etc. Electrodeposition is widely used in making metallic coatings. When deposition is confined inside the pores of template membrane nanocomposites are produced. If the
template membrane is removed nano rods or nano wires are prepared. In nano technology the aim is to place only single layer or more of coverage on a surface by electrodeposition in a controlled way [111-114].

D. Sol-gel synthesis

The sol-gel process as the name implies involves evolution of networks through the formation of a colloidal suspension (Sol) and gelatin of the sol to form a network in a continuous liquid phase (Gel). This process is mainly used to produce metal oxides. They can be synthesized directly in the initial chemical reaction or a metal hydroxide which can be heated to yield the oxides [115-117].

Sol-gel formation occurs in four steps.

➢ Reaction of the appropriate chemical precursor to form colloidal particles.
➢ Aggregation of particles to form gel.
➢ Drying of a gel
➢ Heating to induce phase transformation/densifica

E. Ball milling

Early nanomaterials were made by a simple method called ball milling, which is better described as mechanical crushing. In this process, small balls are allowed to rotate around the inside of a drum and drop with gravity force onto a solid enclosed in the drum. Ball milling breaks down the structure into nanocrystallites. The significant advantage of this method is that it can be readily implemented commercially. Ball milling can be used to make a variety of new carbon types, including carbon nanotubes. This method is preferred for preparing metal oxides [118].
F. Microwave technique

Microwave heating is fundamentally different from conventional processes. In the microwave process, heat is generated internally within the material instead of heat from external source. Microwave energy is widely used to process a variety of ceramic materials. They are transparent to microwaves at ambient temperatures. Microwave chemistry generally relies on the ability of the reaction mixture to efficiently absorb microwave energy taking advantage of “microwave dielectric heating” phenomena such as dipolar polarization or ionic conduction mechanisms [119-121].

G. Co-precipitation method

This involves dissolving a salt precursor (chloride, nitrate, etc.) in water (or other solvent) to precipitate the oxo-hydroxide form with the help of a base. Very often, control of size and chemical homogeneity in the case of mixed-metal oxides are difficult to achieve. Many of the earliest synthesis of nanoparticles were achieved by the coprecipitation of sparingly soluble products from aqueous solutions followed by thermal decomposition of those products to oxides. Coprecipitation reactions involve the simultaneous occurrence of nucleation, growth, coarsening and/or agglomeration processes. However, the use of surfactants, sonochemical methods, and high-gravity reactive precipitation appear as novel and viable alternatives to optimize the resulting solid morphological characteristics [122, 123].

H. Hydrothermal method

Hydrothermal reactions make changes in the earth’s crust leading to the formation of rocks and minerals. An understanding of the mineral formation in nature in the presence of water under elevated temperature and pressure led to the development of the
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hydrothermal technique. Hydrothermal researcher needs a high temperature and high-pressure apparatus called “autoclaves” or “bombs”. At present, one can get many kinds of autoclaves to cover different range of pressure-volume-temperature (PVT). Water is the most important solvent for most ionic compounds. The basic principle behind hydrothermal synthesis is that small crystals will homogeneously nucleate and grow from solution when subjected to high temperatures and pressures. During the nucleation and growth process, water is both a catalyst and occasionally a solid-state phase component. Under the extreme conditions of the synthesis vessel (autoclave or bomb), water often becomes supercritical, thereby increasing the dissolving power, diffusivity, and mass transport of the liquid by reducing its viscosity. In addition, the ability to tune the pressure of the vessel provides an avenue to tailor the density of the final product. When compared to other methodologies, hydrothermal synthesis is environmentally benign, inexpensive, and allows for the reduction of free energies for various equilibria. Materials that are made hydrothermally are generally high-quality, single crystals with a diversity of shapes and sizes. Although, hydrothermal synthesis is an established synthesis route within the ceramics industry, it has recently been rekindled within the scientific community by synthesizing one-dimensional nanostructures, such as carbon nanotubes and oxide nanowires [124, 125].

1.15 DOPING OF NANO SEMICONDUCTORES

The reasons why semiconductors can have electrical conductivity is that the band gap of semiconductors is relatively small. Therefore, electrons can be excited to the conduction band easily. There are two types of semiconductors, intrinsic and extrinsic. An intrinsic semiconductor has its own charge carriers. As the photon must have enough energy to
excite the electron across the band gap, it is not an efficient semiconductor. Extrinsic semiconductors have impurities, also called dopants [126]. The specific properties of a semiconductor depend on the impurities or dopants, added to it. An \textit{n-type} semiconductor carries current mainly in the form of negatively-charged electrons, in a manner similar to the conduction of current in a wire. A \textit{p-type} semiconductor carries current predominantly as electron deficiencies called holes. A hole has a positive electric charge, equal and opposite to the charge on an electron. In a semiconductor material, the flow of holes occurs in a direction opposite to the flow of electrons, which increase their electrical conductivity.

The excitons of semiconductor nanocrystals are confined to all three spatial dimensions which lead to an increase in the effective band gap of the material with decreasing particle size. The nanoscale size range corresponds to the regime of quantum confinement. This phenomenon is known as the quantum size effect. As quantum dot’s radius is smaller than the exciton Bohr radius, it constitutes a class of materials intermediate between molecular and bulk forms of matter. Due to quantum size effect, as the size of quantum dot decreases, the energy gap increases, and more energy is needed to excite the dot while more energy is released when the crystal returns to its ground state, thus resulting in a shift from red to blue for the emission wavelength [127, 128].

Semiconductor with a very large band gap, such as TiO\textsubscript{2} and ZnO, can be employed to construct solar cells. But these materials can only be excited by ultraviolet or near-ultraviolet radiation that occupies only about 4% of the solar light. Dye molecules as light absorbers for energy conversion have shaped evolution via the process of photosynthesis and photo-sensoric mechanisms. Dye sensitization of semiconductor with
a wide band-gap has provided a successful solution to extending the absorption range of the cells to long wavelength region. This approach also presents advantages over the direct band-to-band excitation in conventional solar cells, since attached dyes, rather than the semiconductor itself, are the absorbing species. Importantly, light absorption and charge carrier transport are separated and the charge separation takes place at the interface between semiconductor and sensitizer, preventing electron–hole recombination [129].

The energy conversion efficiency achievable depends on many factors, such as:

➢ The bulk properties of the semiconductor (i.e., Band gap energies and flat-band potentials) and the structure of the film (i.e., crystallite size, porosity and roughness factor).

➢ The photophysical properties of the dye (i.e., LUMO and HOMO positions, extinction co-efficient) and the mode of anchoring of the dye molecules to the semiconductor surface.

➢ The nature of the semiconductor.

➢ The structure of the semiconductor (i.e. nanoparticles, nanotubes, thin films or nanorods) [130].

Focussing on the nature of semiconductor, one way of achieving improvements in the properties of DSSC is by doping of semiconductors. The most common semiconductors used in DSSC are TiO₂ and ZnO. The efficiency of these semiconductors are well known, as are the improvements gained by doping to get different structure with different elements. For example, the following elements have been used as dopants: iron [131-133], chromium [134], carbon [135, 136], nitrogen [137], bismuth [138] or copper [139].
Likewise, studies in the literature have also reported the doping of TiO₂ for the use in DSSCs and reported the improved efficiency of DSSCs made from nanocrystalline films of TiO₂ doped with copper and sensitized with indoline dye. Rare-earth ions are positive trivalent cations, when they are doped in semiconductor TiO₂ and ZnO, a p-type doping effect occur [140-143], which results in the elevation of electron energy level of the photoanode and in turn to the enhancement of photovoltage of DSSCs [144-146]. Particles of TiO₂ or ZnO were doped with one or more suitable dopants such manganese, copper, vanadium, chromium, cerium, selenium, iron, nickel, tin, aluminum, lead, silver, zirconium, zinc and cobalt. The surface-doped particles of the present invention can be obtained by combining particles of a host lattice (TiO₂) with a second component in the form of a salt solution in water and then baking it, typically at a temperature of at least 300 °C and then calcining it at a higher temperature, for example at least 500 or 600 °C. There are three different main opinions regarding modification mechanism of semiconductors doped with metals: (1) Band gap narrowing; (2) Impurity energy levels; and (3) Oxygen vacancies [147]. In considering nanostructured materials, the nanoparticles of TiO₂ are still predominant in achieving the maximum conversion efficiencies nowadays. This is attributed to a large surface area contributed by the nanoparticles and the exposed (1 0 1) planes of TiO₂ nanoparticles which may yield ideal chemisorption with those existing dyes. A further decrease in the nanoparticle size can indeed lead to an increase in the surface area of photoelectrode film. However, due to a simultaneous decrease in the pore size and increase in the defect sites and grain boundaries, use of smaller nanoparticles would eventually lower the solar cell performance. This is also the reason that optimum size for the TiO₂ nanoparticles has
been reported to be in the range of 12-20 nm [148-151]. Surface modification or doping into the TiO$_2$ lattice has also shown superior reproducibility. Therefore, it seems that there is only limited room for improving the solar cell performance by optimizing the photoelectrode film made of nanoparticles. There have been more and more efforts devoted to investigate the doped counterparts. For semiconductors, doping is a powerful tool to tailor the electrical and optical properties. Metal doping modifies the photoluminescent transitions in ZnO and TiO$_2$ by creating localized impurity levels. Doping the impurity ion is known as one of the effective ways to manipulate the internal properties of host material such as crystalline structure and crystallite size [151-155].

1.16 SEMICONDUCTORS IN DYE-SENSITIZED SOLAR CELLS

The solar energy-to-electricity conversion efficiency for the best DSSCs has now been enhanced from 7 to 11%, with various recent efforts directed mainly towards developing better inorganic electrode materials and organic sensitizers. Basically, DSSCs are built upon nanocrystalline semiconductor electrodes sensitized by a dye that absorbs the light and injects electrons into the conduction band of the semiconducting oxide (usually TiO$_2$). In DSSCs, semiconductor oxides have been applied as the main active layer as electron transport materials and as interfacial layers in solar cells [156, 157].

A dye-sensitized solar cell (DSSC) is a type of photoelectrochemical (PEC) solar cell which has been studied extensively [158-161]. In a DSSC, dye molecules are used to sensitize wide-band gap semiconductors, such as TiO$_2$ and ZnO, which assist in separating electrons from photoexcited dye molecules. The visible light absorbed by dye molecules is more intensive than the UV light absorbed by wide-band gap semiconductors, even if the energy of visible light is lower than that of UV light. The
sensitization of wide-band gap semiconductors by adsorbed monolayers of dye molecules began in the late 1960s with the work of Gerishcer [162] and Memming [163]. A conceptual and practical breakthrough occurred in the late 1980s when Gratzel and coworkers started using high-surface-area semiconductors for DSSCs [164-166].

The mechanism of solar cell devices is based upon the injection of an electron from a photo-excited state of the sensitized dye into the conduction band of the semiconductor. The efficiency of the dye-sensitized solar cells depends critically on the rates of the forward (dye-to-semiconductor) and back (semiconductor-to-dye) electron transfer reactions. For an efficient solar energy conversion, it is necessary to establish conditions for both fast electron injection and slow recombination. High yield of long-lived charge separation is expected for useful conversion of sunlight into electric charge. To gain higher efficiency in the devices it is very important to pacify these surface states. Surface modification of semiconductor nanoparticles changes their optical, chemical and photocatalytic properties significantly. It can lead to the following effects [167-171]:

- It may enhance their excitonic and defect emission by blocking non-radiative electron/hole (e⁻/h⁺) recombination at the defect sites (traps) on the surface of the semiconductor nanoparticles.
- It may enhance the photo-stability of semiconductor nanoparticles.
- It may create new traps on the surface of the nanoparticles leading to the appearance of new emission bands.
- It may enhance the selectivity and efficiency of light-induced reactions occurring on the surface of semiconductor nanoparticles.
In a dye-sensitized photoelectrode, dye molecules play a critically important role in absorbing the incident photons and then generating photoexcited electrons, which finally transfer to the oxide through an electron injection. To well fulfill these functions, the dye molecules must simultaneously meet several requirements, including (1) forming chemisorption bonds with the oxide, (2) large extinction coefficient and broad absorption spectrum in the visible region, (3) suitable excited state energy level relative to the conduction band of the oxide, (4) sufficient life-time at excited state so as to allow for effective electron transfer, and (5) long term stability for many million cycles [172].

In DSSCs, the choice of semiconductor is constrained by several factors. First, the semiconductor must have conduction band energy and density of states that allow efficient electronic coupling with the dye energy levels to facilitate charge separation and minimize recombination. Second, the semiconductor morphology must present high surface area to maximize light absorption by the dye monolayer while maintaining good electrical connectivity to the substrate [173].

An impressive breakthrough of DSSC, as is well known, was made by Gratzel et al. in 1991 using semiconductor films consisting of nanometer-sized TiO$_2$ particles sensitized with a trimeric ruthenium complex, announcing overall conversion efficiencies of 7.1-7.9% [174]. On one hand, such an achievement of high conversion efficiency is a result of the use of a newly developed dye at that time, RuL$_2$(μ-(CN)Ru(CN)L$_2$)$_2$, L=2,2′-bipyridine-4,4′-dicarboxylic acid, L=2,2′-bipyridine), which possesses high extinction coefficients and broad absorption spectrum with the onset at 750 nm. On the other hand, the use of crystalline nanoparticles to form photoelectrode film is also a critically
Important reason that introduces a way of yielding an extremely large internal surface for
dye adsorption [175].

In the recent years, many attempts using different modifications of the originally
proposed cell have been made in order to improve its performance, most of them based
on the use of different semiconductors [176], dyes [177] or ionic conductors [178].
However, the extremely delicate sensibility of the charge transport and recombination
dynamics to any alteration of the nature of the interfaces present in the cell should be
considered [179]. For instance, some of the most important routes of research have
focused on the molecular engineering of suitable dyes having broader absorption spectra
that show a better matching to the solar spectrum and higher molar extinction coefficients
[177], thus yielding higher short circuit currents.

1.17 RECENT DEVELOPMENTS IN DSSC

Since their discovery, progress in DSSCs can be divided into five categories: sensitizers,
counter electrodes, electrolytes, semiconductors and structural changes. Improvements in
these components have been performed to address specific aspects of DSSCs such as
light absorption, electron and hole transport, sealing and stability issues as well as
preventing recombination. The following section will briefly describe some trends in
these categories, followed by a more detailed analysis of structural changes in DSSCs
[180, 181].

Counter electrode progress has been mainly driven by the replacement of
platinum. A key selling point of DSSCs is their low cost. At the current price, platinum
substitution is an easy way to produce more economical solar cells. Recent examples of
substitutes include carbon counter electrodes, metal counter electrodes as well as CoS
counter electrodes. One of the advantages of platinum is that it can be applied in very thin films, allowing transparent counter electrodes to be made - a valuable feature which may someday be used to allow for tandem cells or solar harvesting windows.

Electrolyte solutions have for the most part remained quite unchanged over the past decade. Most of the commercial electrolytes are proprietary and there are few reports of electrolyte optimization. Electrolytes are usually customized according to the valence band and conduction band of the sensitizers used and thus as new dyes keep emerging into the market, so do the electrolyte mixtures. Electrolyte solutions include Iodide and Iodine in Acetonitrile as well as additives such as lithium or pyridines which have been shown to prevent recombination as well as modify the redox potential of the electrolyte solution. A typical electrolyte solution consists of 0.6 M Tetrabutylammonium Iodide, 0.1 M Lithium Iodide, 0.5 M 4-Tetra-butylpyridine and 100 mM Iodine in Acetonitrile. Due to the volatile nature of the Acetonitrile electrolyte, there has been a push to use alternative electrolyte solutions including ionic liquids, eutectic melts, water and solid state charge transporters [182-184]. Although ionic liquids have reached 7% efficiency, they have been shown to be unstable under prolonged thermal stress and light soaking. Eutectic melts have recently been shown to reach 8.2% by the Gratzel group which has sparked a flurry of interest in this field [182-185].

DSSCs based on nanowire/nanorod arrays have been reported to exhibit improved electron transport efficiency. Intensity-modulated photovoltage and photocurrent spectroscopies have revealed that photoanode based on ZnO nanorod arrays exhibits two orders of magnitude faster electron transport while retaining similar electron recombination time compared to photoanodes based on nanoparticles [186]. However, the
photocurrents and the efficiencies of the nanowire/nanorod-based DSSCs are limited by insufficient surface area for dye adsorption. To further improve the performance of DSSCs, various structures, such as branch structure [187], nanoflower [188], and hybrid nanowire/nanoparticle [188, 189, 190] have been employed as the photoanodes to achieve fast electron transport while maintaining a large surface area for dye coating.

DSSCs have kept their efficiency record at 10-11% for many years, which are however far lower than the theoretically predicted one [191]. In principle, there are two potential ways that may achieve a breakthrough in the conversion efficiency of DSSCs. One way is to reduce the energy loss in the solar cell caused by, for example, charge recombination, electron trapping, optical reflection, and so on. In this regard, nanotechnology with capability of tailoring materials for defined purpose may create abundant nanostructures, and with these nanostructured materials it is possible to receive increased electron diffusion length, decreased back recombination, and physical effects such as photon localization, thus a decrease in the energy loss would likely lead to an improvement in the solar cell efficiency. Another way based on a consideration of boosting the light harvesting efficiency of photoelectrode is to develop new photosensitizers with higher molar extinction coefficient and broader spectral response than the existing dyes. This point has been well manifested to be both direct and effective by the history and development of DSSCs over the past decades. Of course, the chemists have never stopping seeking for more powerful photosensitizers including organic dyes and other types, for example, quantum dots and energy relay dyes [192-194].

Many semiconductors are used as $p$-type materials and researchers reported many synthesis methods to change the structural, electrical and optical properties of
semiconductors. In this present work, metal doped nano semiconducters were synthesized using relatively simple methods. Films were fabricated based on doped semiconductors and sensitized with various dyes. Optical properties of dye-sensitized films were characterized using UV-Vis spectroscopy.
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