NANOMATERIALS FOR SMART ENERGY SYSTEMS: FROM LED TO SUPERCAPACITORS AND SOLAR CELLS.

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Abstract: It has been forecast that there will be a severe impact on world economics and ecology in future by energy consumption/production that rely on the combustion of fossil fuels. Therefore more sustainable and more environmentally friendly alternative energy/power generation sources are currently under serious consideration. One such alternative is electrochemical energy production. Systems for electrochemical energy storage and conversion include batteries, fuel cells and electric double layer capacitors (EDLCs). Although the energy storage and the conversion mechanisms are different, there are "electrochemical similarities" of these three systems. Electric double layer capacitors, also known as supercapacitors or ultracapacitors, have tremendous potential as high energy high power sources for use in low weight hybrid systems. Commercial applications for such devices include uninterruptible power applications, telecommunication and transportation. The total energy stored in a conventional capacitor is proportional to both the number of charges stored and the potential between the plates. Essentially the former is a function of the size of the electrode while the later is determined by the breakdown of dielectric between the plates. Different voltages, hence energy stored, can be generated when different dielectric materials are used to separate the plates. Materials can be optimized to produce high energy densities for a given size of a capacitor. In contract to conventional capacitors, supercapacitors do not have a conventional dielectric. Instead, two layers of the same substrate and their electrical properties are used in order to effectively separate the charges despite vanishingly thin (on the order of nanometer) physical separation of the layers. Higher energy storage density can be achieved in supercapacitors when nanomaterials or materials with nanoporous structure are used because such materials offer enormous surface to volume ratio.

Activated carbon is a material with unique properties especially in relation to its nanoporosity and can therefore be used in supercapacitors. Sri Lanka is one of the worlds' best coconut shell based activated carbon producer. Besides, carbon nanotube (CNT, either MWCNT or SWCNT) can also be used in supercapacitors as electrode material where charge storage capacity can be increased to a much higher value. Ceylon vein graphite is a good source for the production of CNT. Further, the use of nano-TiO_2 in conjunction with light absorbing material in cost effective solar cells is a well established process. The charge carrier generation process in solar cells mimics natural photosynthesis (green energy). At present such solar cells have efficiency nearly 11 %. Again Sri Lanka inherits a vast naturally occurring TiO_2 deposit, the range of benefits of which is yet to be explored and harvested to produce nano-TiO_2. Therefore nanomaterials in Sri Lanka has a wide spectrum of application and in this presentation, the opportunities to develop smart energy systems using Sri Lankan nanomaterials will be presented.

Keywords: Sustainable energy, Supercapacitors, Carbon nanotube, Titanium Dioxide, Dye-sensitized Solar Cells, Activated Carbon, anatase-TiO_2, carbon nanotube, graphene.

1. Introduction

"Clean" energy generation and storage is a fascinating area of research. It encompasses many different disciplines varying from biology to physics posing scientifically challenging yet interesting issues. Clean energy generation reinforces the idea of reduction of carbon footprints and gathers momentum to the search of a lasting solution to the world energy crisis. "BP Statistical Review of World Energy" [1] predicts that the petroleum reserve may sufficient to meet the consumption requirements for just over four decades which emphasizes the necessity of coherent research efforts on alternative energy resources for energy generation. Among the alternative energy resources for "clean energy generation", solar energy is far more attractive and important because of its low environmental impact and the abundance. Therefore the research on solar cells has attracted a great deal of interest within the scientific community. Similarly, there is a growing interest to develop new systems/devices for energy storage. In particular, energy storage via capacitors, precisely *via* supercapacitors, has stimulated research efforts in the area of electrochemical energy production. Systems for electrochemical energy storage and conversion include batteries, fuel cells and electric double layer capacitors (EDLCs). Although the energy storage and the conversion mechanisms are different, there are "electrochemical similarities" of these three systems [2].

Electric double layer capacitors, also known as supercapacitors or ultracapacitors, have tremendous potential as high energy high power sources for use in low weight hybrid systems [3-5]. Commercial applications for such devices include uninterruptible power applications, telecommunication and transportation. The total energy stored in a conventional capacitor is proportional to both the number of charges stored and the potential between the plates. Essentially the former is a function of the size of the electrode while the later is determined by the breakdown of dielectric between the plates. Different voltages, hence energy stored, can be generated when different dielectric materials are used to separate the plates. Materials can be optimized to produce high energy densities for a given size of a capacitor. In contrast to conventional capacitors, supercapacitors do not have a conventional dielectric. Instead, two layers of the same substrate and their electrical properties are used in order to effectively separate the charges despite vanishingly thin (on the order of nanometer) physical separation of the layers. Higher energy storage density can be achieved in supercapacitors when nano-materials or materials with nanoporous structure are used because such materials offer enormous surface to volume ratio [6].

Undoubtedly the Si based p-n homojunction solar cells invented in 1941 [7] and developed later by many workers [7, 8] are the most efficient photovoltaic devices to date. Mostly benefiting from the advances in the semiconductor industry, the Si based photovoltaic devices are currently fabricated and have now reached efficiency as high as its theoretical limit [9]. However, the economically intractable production cost of Si based photovoltaic devices has restricted their application in large scale. In the past three decades, a great deal of work has been carried out in the field of cost-effective alternative solar energy generation sources. In particular, sensitized nanostructures based solar cells [10-12] have been the main focus area of research. Commonly referred to as “bulk” junctions or mesoscopic injection or exitonic solar cells, they are formed, for example, from nanocrystalline inorganic oxides, ionic liquids, organic hole conductors or conducting polymer devices. As a result of the use of cost-effective routes and materials in their fabrication process, they offer prospects of low cost fabrication without expensive and energy intensive high temperature high vacuum processes. They can credibly be produced employing flexible substrates and are compatible with a variety of embodiments and appearances to facilitate market entry, both for use in domestic devices as well as in architectural or decorative devices. The mesoscopic injection solar cells operate in an entirely different fashion than conventional Si based p-n homo-junction devices. Mimicking the principles of natural photosynthesis that nature has used successfully over the past 3.5 billion years in solar energy conversion [13], they achieve the separation of light harvesting and charge carrier transport. This unique feature distinguishes them from conventional p-n junction devices where both functions are assumed simultaneously imposing stringent conditions for purity and entailing high materials and production cost.

2. Principles, materials, methods and device fabrication.

In a typical sensitized nanostructures based solar cell, a photo-stable high band gap semiconductor (e.g., TiO_2) is used as the electron harvesting component. By following a well established sol-gel route, a colloidal solution of the semiconductor is first prepared and subsequently deposited after concentrating on a transparent conducting tin oxide (CTO) glass using “doctor blade” technique. Then the film is sintered in an air at 450 ^{0}C in order to create a network of interconnected nanostructures on the electrode. As such nanostructure network generates a high surface/volume to ratio, the photoactive surface area of the electrode become much higher than the geometrical surface area. Larger the photoactive area higher the light absorption cross section and hence the photocurrent. As the high-band gap materials are not sensitive to the visible spectrum, the spectral response of the high-band gap materials are extended to the visible region by using either inorganic (e.g., quantum dots QDs) or organo-metallic (metal-organic based dyes such as the N3 dye) dyes. Here it is essential that we select the dye materials whose light absorption properties are in line with the light emission properties of the Sun. In practice, the dye is anchored to the surface of the semiconductor via a solution based deposition process after which the dye is electronically coupled with the semiconductor. A thin layer of electrolyte containing a redox couple (e.g, I^-/I_3^- redox couple) is sandwiched between the semiconductor and a counter electrode. The counter electrode is usually a conducting tin oxide substrate deposited with Pt islets which is also transparent. The Pt islets deposited on CTO substrate catalyze the electron transfer from the electrode to the one half of the redox couple completing the charge cycle in a short circuit conditions.

However, the presence of a liquid electrolyte to shuttle charge carriers between the two electrodes in this cell has disadvantage that the liquid electrolyte vaporizes due to heat generated in the cell when under constant illumination. In addition, it is not possible to seal the two electrodes effectively as a result of the presence of the liquid electrolyte. These two problems were long standing problems in the field of sensitized nanostructures based solar cells until a group of Sri Lankan scientists (one of the authors (ARK) in this paper involved in this work) who were actively working in the field finds a solution in 1995 [14]. A solid p-type hole transport inorganic material was found to behave in a manner similar to the liquid electrolyte used in the cell paving the way of replacing the liquid in the cell. This was a significant finding in the field as it contained all the necessary ingredients to develop a fully solid state dye-sensitized solar cell by introducing a change to the state of the medium present in the cell. In terms of practical application, the solid form is the "only possible form" for a solar cell. The hole transport material, an inorganic metal halide, Copper (1) iodide, CuI, is a high band gap p-type semiconductor. One of the interesting features of this material is being able to deposit it on the dye coated nanocrystalline surface at an elevated temperature without denaturing the delicate monolyer of the dye. When the hole transport materials is deposited on n-TiO_2 coated with Ru metal based dye, a new type of structure is created where a monolayer of light absorbing material is sandwiched between n-type and p-type high bad gap semiconductor materials. Technically, a hetero-junction is formed consisting of n-TiO_2/dye/p-CuI, the behavior of which is entirely different to that in Si based p-n junction solar cells (i.e., in terms of charge carrier generation and separation). The fascinating feature of such hetero-junction interfaces is the discontinuity of the local band structure at the interface which originates as a result of the bringing of two dissimilar semiconductors with different carrier concentrations in contact [15]. Associated to this intriguing feature, hetero-junction interfaces exhibit interesting and useful electronic properties which are functional in solar cells. Similar to the liquid state solar cells, the organo-metallic dye chemically bonded to the n-type nanostructure via an electronic coupling absorbs photons from the incident light and nanostructure harvests the electrons in solid state dye-sensitized solar cells. However it should be mentioned here that the recent investigation carried out by one of the authors (ARK) at this interface using high flux X-ray absorption techniques at ELETTRA, Synchrotron, Trieste, Italy is seemed to suggest that the N3 dye not only bonds (via carboxylate ligands, -Ti-O-C-) with n-type nanostructured TiO_2 but also with p-type CuI (via Cu-N bond). This envisages the possibility that the dye forms a molecular level bridge between the n-TiO_2 and the p-CuI which could possibly act as a conduit for charge transfer. Nevertheless further studies are needed to evaluate the strength of each bond in order to determine whether the formation of –Cu-N- bond breaks the most important –Ti-O-C- bond as it has been speculated that the –Cu-N- may have an influence on the stability of the –Ti-O-C- bond which is the primary charge transfer channel.

Following the injection of the carriers into the bands, the positive charge left behind in the ground state of the dye is rapidly scavenged by the p-type solid hole transport (HTM) material creating a photocurrent in the cell. The open circuit photovoltage of the cell is determined by the difference in work functions between n-TiO_2 and p-CuI which is over 1eV according to the interface band energy diagram [16]. The sensitized nanostructures based solid state solar cells (i.e., n-semi/dye/p-semi) have shown a remarkable progress since its invention [17] and the progress continues [18].

Solar cells generate energy. Once the energy is generated, there should be a way to store it in order to use it later as required. An attractive way of storing energy lies at the heart of electrochemical energy storage methods. Electrochemical energy storage includes batteries, fuel cells and super-capacitors. Out of these possible routes, supercapacitors or EDLCs has surpassed other devices because they can release burst of stored energy when the need arises. Many electronic devices such as laptops, memory backups, mobiles and communication systems require a burst of energy to start up. A German physicist, Hermann von Helmholtz, first described the concept of EDLC in 1853 [19]. Well over 100 years later, in 1957 General Electric (GE) first patented [20] electrochemical capacitor based on the double-layer capacitance structure. Since then, the field of EDLCs has shown an enormous growth to date. The operating principle of supercapacitors is simple and easy to fabricate.

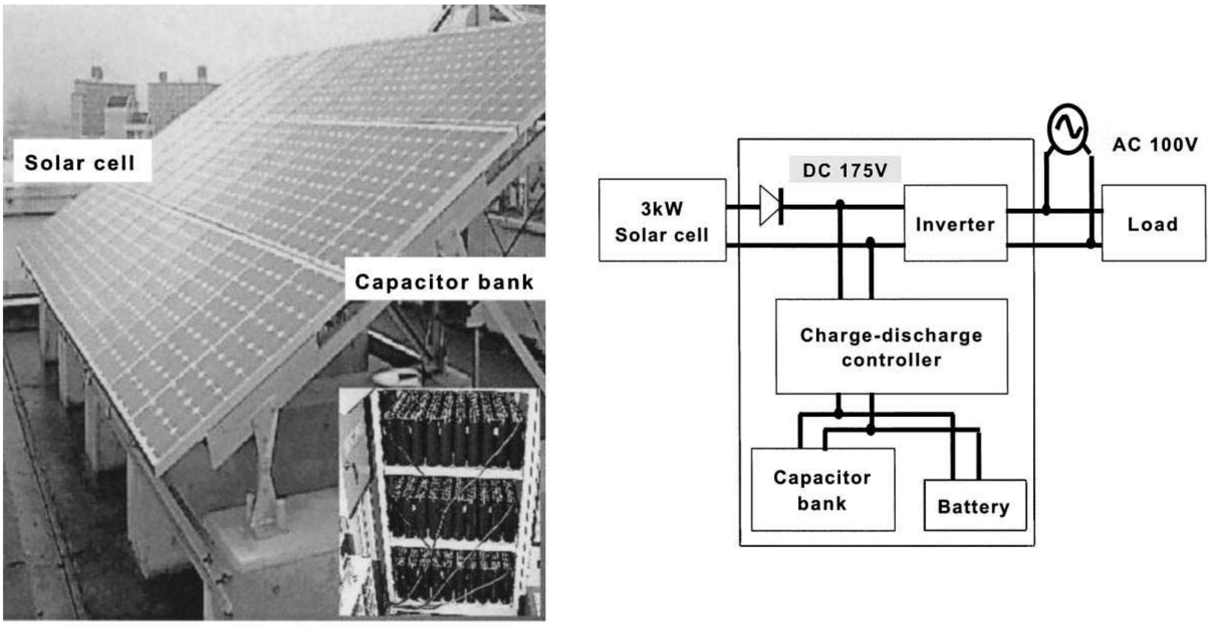
3. Sri Lankan perspectives.

The electrical properties of a super capacitor are determined by the selection of electrode material. Double-layer-charge-storage is a surface process and the surface characteristics greatly influence the capacitance of the cell [21]. Various materials are being used as electrode materials, for example carbon, metal oxides, conducting polymers, hybrid and conducting polymers etc [21]. Carbon has been utilized as high-surface area electrode material ever since the development of double layer capacitor began. Today it is still an attractive material because of its low coat, availability and the long history of use (ref). Carbon electrode can take a number of manufactured forms such as foams, fibers and nanotubes. The use of activated carbon in EDLCs is well established due to its high surface area, e.g., up to 2000 m^2/g. Capacitance up to 5000 F [3] has been reported from commercially available super capacitors produced in USA, Japan and Korea. Research into further develop current numbers using new materials, for example carbon nanotube, are continuing and gaining significant momentum. Besides, dye-sensitized solar cells that use nanocrystalline TiO_2 as the electron harvesting electrode have achieved a remarkable success since its inception. Efficiencies as high as 11.4 % [23] has been achieved with newly developed, thermally stable dyes.

From the point of view of the availability of materials used in these devices, Sri Lanka shows a great promise. The world best coconut shell based activated carbon is produced in SL which can with no doubt go in to develop EDLCs. Vein graphite, one of the naturally occurring forms of graphite which is available only in Sri Lanka in commercial levels is a very good source for making carbon nanotubes to the best of the knowledge of the authors. The vein graphite is also a good resource for making graphite oxide which can be used in nanocomposites, or perhaps even to synthesis the "next generation wonder material graphene" which is expected to be revolutionized the entire electronic industry as Si is reaching its fundamental limits. The significance of graphene has recently been perceived by awarding the highest scientific accolade, the Nobel Prize, for physicists who invented the materials. Moreover, SL has naturally occurring ilmanite ($FeTiO_2$) deposit which can be used to extract titanium dioxide, TiO_2. Credible methodologies have been developed by Sri Lankan scientists who are working in SLINTEC science team at present to convert ilmanite into TiO_2 and then to nano-TiO_2. The use of nano-TiO_2 is multifaceted which includes solar cells, self-cleaning windows, smart clothing, paints, cosmetics, catalysis and many more. Therefore, building a sustainable environment with smart energy systems developed using nanomaterials available in SL is a promising target that has a long range benefits to the Sri Lankan economy.

4. Conclusion

The building environment consumes huge fraction of energy produced in any social system. Therefore the significance of a sustainable built environment in terms of energy is invaluable and scientific and administrative efforts aimed at achieving such an environment should be recognized as a priority issue. The potential of nanotechnology to answer world's current and future burning issues (energy crisis one of them) is great and the scale that one can use the nanotechnology based products spans across a wide a spectrum. When the materials required to develop nanotechnology based devices are liberally available/or the raw materials that can be used to extract such materials are available, the journey to achieve the targets set out in a sustainable built environment is becoming more quicker, easier and also is cost effective. Therefore to build a sustainable built environment, nanomaterials available in Sri Lanka can contribute in a substantial and innovative way. Finally the inquisitive nature of mankind has invented many novel things/methodologies devices in the world up to its development and the quest continues.



(a) Appearance of the system **(b) Construction of the system**

Photo and schematic diagram showing how solar cells and EDLCs could be used in a building environment (Ref. J. Power Sources, 97-98, 2001, 807-811)

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