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Flexible Photovoltaic Textiles for Smart Applications

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1. Introduction

In recent years alternative renewable energies including that obtained by solar cells have attracted much attention due to exhaustion of other conventional energy resources especially fossil-based fuels. Photovoltaic energy is one of the cleanest, most applicable and promising alternative energy using limitless sun light as raw material. Even though, inorganic solar cells dominate in the world photovoltaic market, organic solar cells as the new emerging photovoltaics has explored new possibilities for different smart applications with their advanced properties including flexibility, light-weight, and graded transparency. Low cost production and easy processing of organic solar cells comparing to conventional silicon-based solar cells make them interesting and worth employing for personal use and large scale applications . Today, the smart textiles as the part of technical textiles using smart materials including photoactive materials, conductive polymers, shape memory materials, etc. are developed to mimic the nature in order to form novel materials with a variety of functionalities. The solar cell-based textiles have found its application in various novel field and promising development obtaining new features. These photovoltaic textiles have found its application in military applications, where the soldiers need electricity for the portable devices in very remote areas. The photovoltaic textile materials can be used to manufacture power wearable, mobile and stationary electronic devices to communicate, lighten, cool and heat, etc. by converting sun light into electrical energy. The photovoltaic materials can be integrated onto the textile structures especially on clothes, however, the best promising results from an efficient photovoltaic fiber has to be come which can constitute a variety of smart textile structures and related products[1].

Fossil fuels lead to the emission of CO_2 and other pollutants and consequently human health is under pressure due to adverse environmental conditions. In consequence of that renewable energy options have been explored widely in last decades[2-3].

Unprecedented characteristics of photovoltaic (PV) cells attract maximum attention in comparision of other renewable energy options which has been proved by remarkable growth in global photovoltaic market[4].

Organic solar cells made of organic electronic materials based on liquid crystals, polymers, dyes, pigment etc. attracted maximum attention of scientific and industrial community due to low weight, graded transparency, low cost, low bending rigidity and environmental friendly processing potential[5-6]. Various photovoltaic materials and devices similar to solar cells integrated with textile fabrics can harvest power by translating photon energy into electrical energy.

2. Driving forces to develop organic PV cells

Energy is the greatest technological problem of the 21st century. Energy conversion efficiency is a dominant factor to meet the increasing demand of energy worldwide. Solar energy looks easy alternative next to conventional sources, like electricity, coal and fuels. The use of solar energy can become more popular by developing photovoltaic (PV) cells of improved efficiency. The crystalline silicon PV cells are 12 % efficient with very high manufacturing cost. Thin-film cells based on CdTe, $CuInS_2$ and amorphous Si are promising, but In is expensive, Cd is toxic and amorphous Si isn't stable. A 10 % efficient cell can generate energy level equivalent to 100 W/m^2. Recently, the development of photovoltaic fibre, a great innovation in the field of photovoltaics made the technology more attractive and smart[7-12].

3. Classification of solar cells

Author has made an effort to classify the available solar cells.

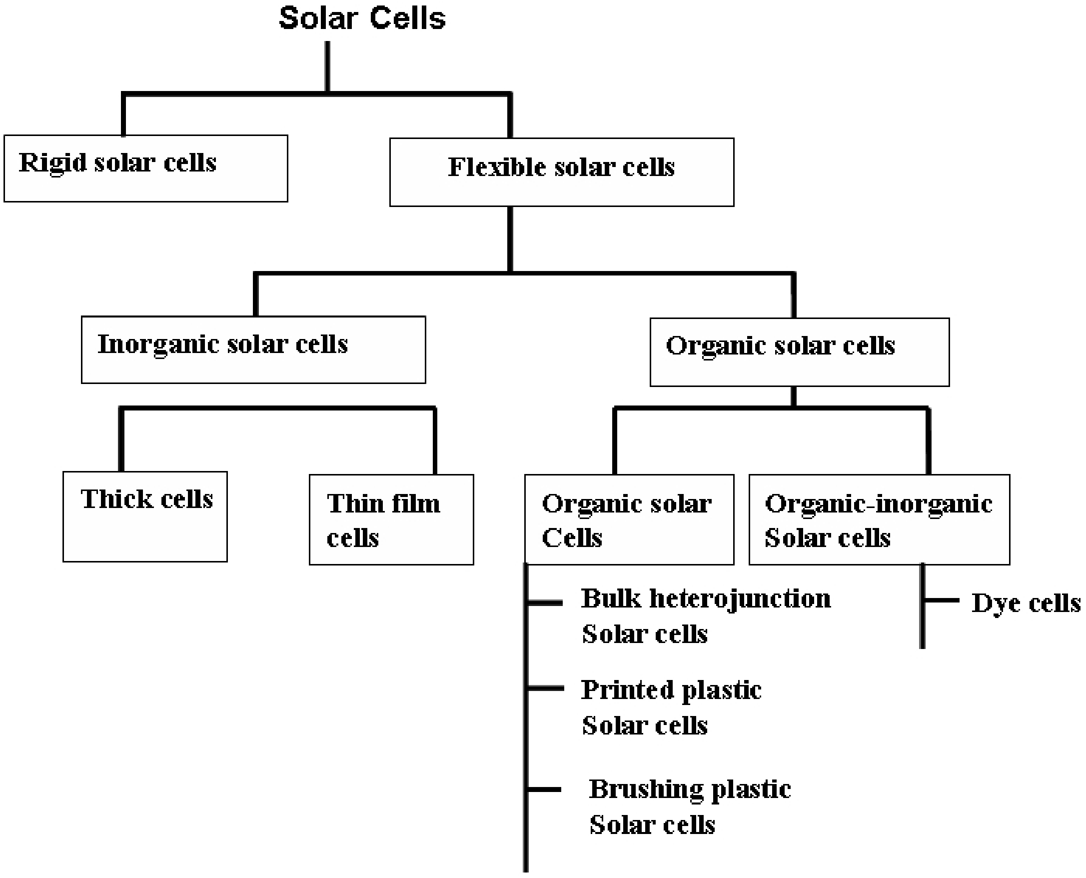

Fig. 1. Classification of Solar cells

Organic solar cells are discussed in detail in this chapter due to their higher compatibility to develop photovoltaic textiles.

4. Manufacturing of organic photovoltaic cells

Indium tin oxide (ITO) was used as a common transparent electrode in polymer-based solar cells due to its remarkable efficiency and ability of light transmission. However, it is quite expensive and generally too brittle to be used with flexible textile substrates. Therefore, highly conductive poly (3,4-ethylenedioxythiophene) doped with poly(styrene sulfonate) PEDOT:PSS, carbon nano-tube or metal layers are used to substitute ITO electrode. This can be a promising way to develop PV textiles for smart application due to its low cost and easy application features for future photovoltaic textile applications. A typical sequence of photovoltaic textiles manufacturing is exhibited in Fig. 2.

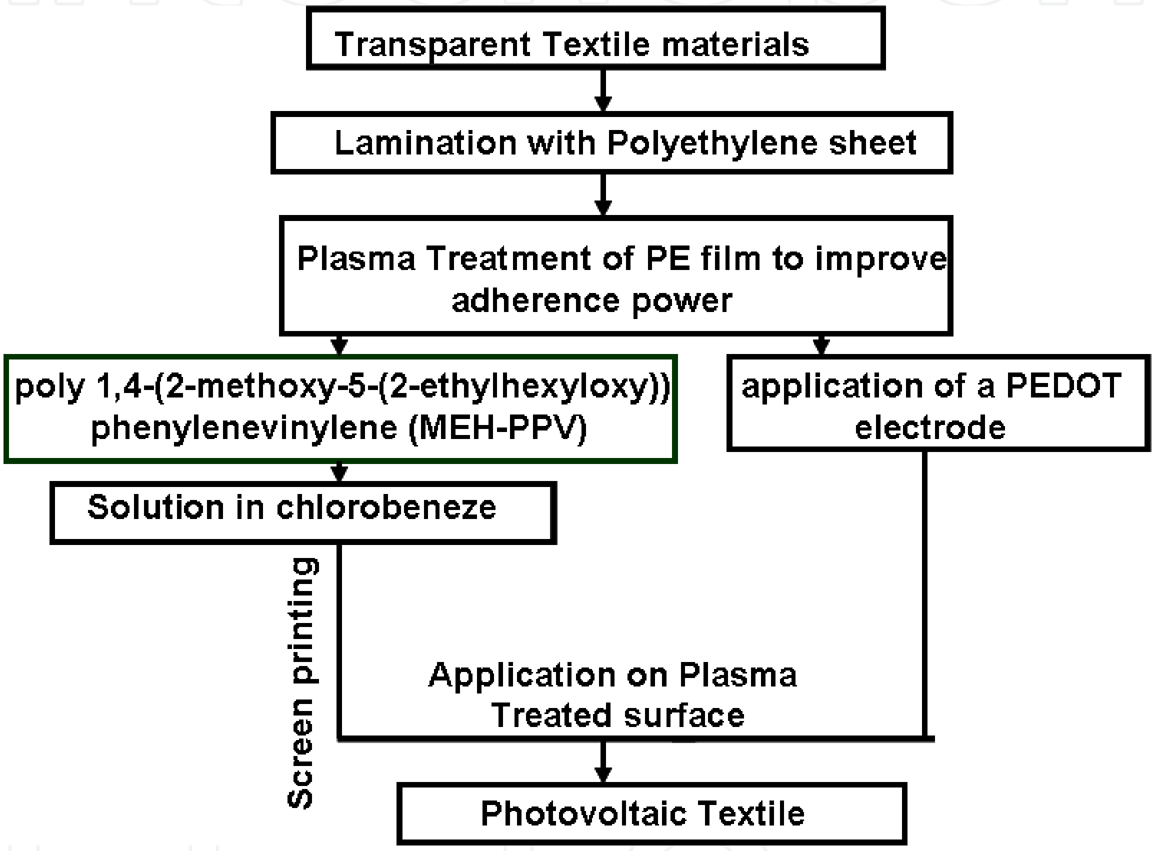

Fig. 2. A typical sequence of photovoltaic textiles manufacturing

A group of scientists has demonstrated the fabrication of an organic photovoltaic device with improved power conversion efficiency by reducing lateral contribution of series resistance between subcells through active area partitioning by introducing a patterned structure of insulating partitioning walls inside the device. Thus, the method of the present invention can be effectively used in the fabrication and development of a next-generation large area organic thin layer photovoltaic cell device[13].

The manufacturing of organic photovoltaic (PV) cells can be possible at reasonable cost by two techniques:

4.1 Roll-to-roll coating technique

A continuous roll-to-roll nanoimprint lithography (R2RNIL) technique can provide a solution for high-speed large-area nanoscale patterning with greatly improved throughput. In a typical process, four inch wide area was printed by continuous imprinting of nanogratings by using a newly developed apparatus capable of roll-to- roll imprinting (R2RNIL) on flexible web base. The 300 nm line width grating patterns are continuously transferred on flexible plastic substrate with greatly enhanced throughput by roll-to- roll coating technique.

European Union has launched an European research project "HIFLEX" under the collaboration with Energy research Centre of the Netherland (ECN) to commercialize the roll to roll technique. Highly flexible Organic Photovoltaics (OPV) modules will allow the cost-effective production of large-area optical photovoltaic (OPV) modules with commercially viable Roll-to-Roll compatible printing and coating techniques.

Coatema, Germany with Renewable Technologies and Konarka Technologies has started a joint project to manufacture commercial coating machine. Coatema, Germany alongwith US Company Solar Integrated Technologies (SIT) has developed a process of hot-melt lamination of flexible photovoltaic films by continuous roll-to-roll technique[14]. Roll-to-roll (R2R) processing technology is still in neonatal stage. The novel innovative aspect of R2R technology is related to the roll to roll deposition of thin films on textile surfaces at very high speed to make photovoltaic process cost effective. This technique is able to produce direct pattern of the materials[15, 16].

4.2 Thin -film deposition techniques

Various companies of the world have claimed the manufacturing of various photovoltaic thin films of amorphous silicon (a-Si), copper indium selenide (CIGS), cadmium telluride (CdTe) and dye-sensitized solar cell (DSSC) successfully. Thin film photovoltaics became cost effective after the invention of highly efficient deposition techniques. These deposition techniques offer more engineering flexibilities to increase cell efficiencies, reflectance and dielectric strength, as well as act as a barrier to ensure a long life of the thin film photovoltaics and create high vapour barrier to save the chemistry of these types of photovoltaics[17-18].

A fibre shaped organic photovoltaic cell was produced by utilizing concentric thin layer of small molecular organic compounds as shown in Fig 3.

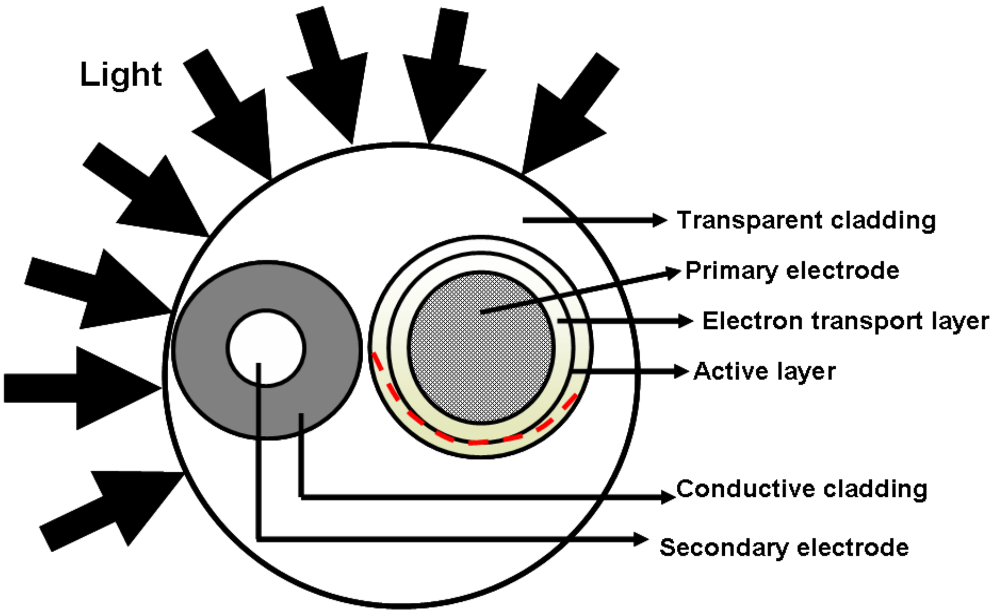

Fig. 3. Photovoltaic fibre

Thin metal electrode are exhibited 0.5% efficiency of solar power conversion to electricity which is lower than 0.76% that of the planner control device of fibre shape organic PV cells. Results are encouraged to the researchers to explore the possibility of weaving these fibres into fabric form.

4.2.1 Dye-sensitized photovoltaics

An exhaustive research on photovoltaic fibres based on dye-sensitized TiO_2-coated Ti fibers has opened up various gateways for novel PV applications of textiles. The cohesion and adhesion of the TiO_2 layer are identified as crucial factors in maintaining PV efficiency after weaving operation. By proper control of tension on warp and weft fibres, high PV efficiency of woven fabrics is feasible.

The deposition of thin porous films of ZnO on metalized textiles or textile-compatible metal wires by template assisted electro-deposition technique is possible. A sensitizer was adsorbed and the performance as photoelectrodes in dye-sensitized photovoltaic cells was investigated. The thermal instability of textiles restricts its use as photovoltaic material because process temperatures are needed to keep below 150°C. Therefore, the electro-deposition of semiconductor films from low-temperature aqueous solutions has become a most reliable technique to develop textile based photovoltaics. Among low-temperature solution based photovoltaic technologies; dye sensitized solar cell technology appears most feasible. If textile materials are behaved as active textiles, the maximum electrode distance in the range of 100 µm has to be considered. Loewenstein et al., (2008) and Lincot et al., (1998) have used Ag coated polyamide threads and fibers to deposit porous ZnO as semiconductor material . The crystalline ZnO films were prepared in a cathodic electrodeposition reaction induced by oxygen reduction in an aqueous electrolyte in presence of Zn^{2+} and eosinY as structure-directing agent[19-20].

Bedeloglu et al., (2009)[21] were used nontransparent non-conductive flexible polypropylene (PP) tapes as substrate without use of ITO layer. PP tapes were gently cleaned in methanol, isopropanol, and distilled water respectively and then dried in presence of nitrogen. 100nm thick Ag layer was deposited by thermal evaporation technique. In next step, a thin layer of poly(3,4-ethylenedioxythiophene) doped : poly(styrene sulfonate) PEDOT: PSS mixture solution was dip coated on PP tapes. Subsequently, poly [2-methoxy-5-(3, 7-dimethyloctyloxy)-1-4-phenylene vinylene] and 1-(3-methoxycarbonyl)-propyl-1-phenyl(6,6)C61, MDMO: PPV: PCBM or poly(3-hexylthiophene) and 1-(3-methoxycarbonyl)-propyl-1-phenyl(6,6)C61, P3HT: PCBM blend were dip coated onto PP tapes. Finally, a thin layer of LiF (7nm) and Al (10nm) were deposited by thermal evaporation technique.

The enhanced conductivity will always useful to improve the photovoltaic potential of poly(3,4-ethylene dioxythiophene):poly(styrene sulfonate) (PEDOT:PSS). Photovoltaic scientific community found that the conductivity of poly(3,4-ethylene dioxythiophene): poly(styrene sulfonate) (PEDOT:PSS), film is enhanced by over 100-folds if a liquid or solid organic compound, such as methyl sulfoxide (DMSO), N,Ndimethylformamide (DMF), glycerol, or sorbitol, is added to the PEDOT:PSS aqueous solution. The conductivity enhancement is strongly dependent on the chemical structure of the organic compounds. The aqueous PEDOT: PSS can be easily converted into film form on various substrates by conventional solution processing techniques and these films have excellent thermal stability and high transparency in the visible range[22-25].

Some organic solvents such as ethylene glycol (EG), 2-nitroethanol, methyl sulfoxide or 1-methyl-2-pyrrolidinone are tried to enhance the conductivity of PEDOT: PSS. The PEDOT:

PSS film which is soluble in water becomes insoluble after treatment with EG. Raman spectroscopy indicates that interchain interaction increases in EG treated PEDOT: PSS by conformational changes of the PEDOT chains, which change from a coil to linear or expanded-coil structure. The electron spin resonance (ESR) was also used to confirm the increased interchain interaction and conformation changes as a function of temperature. It was found that EG treatment of PEDOT: PSS lowers the energy barrier for charge among the PEDOT chains, lowers the polaron concentration in the PEDOT: PSS film by w 50%, and increases the electrochemical activity of the PEDOT: PSS film in NaCl aqueous solution by w100%. Atomic force microscopy (AFM) and contact angle measurements were used to confirm the change in surface morphology of the PEDOT: PSS film. The presence of organic compounds was helpful to increase the conductivity which was strongly dependent on the chemical structure of the organic compounds, and observed only with organic compound with two or more polar groups. Experimental data were enough to make a statement that the conductivity enhancement is due to the conformational change of the PEDOT chains and the driving force is the interaction between the dipoles of the organic compound and dipoles on the PEDOT chains[26].

Thin film PV structure offers following advantages [27-29]:

- Photovoltaic thin film structures are more efficient in comparison to their planar counterparts.
- Photovoltaic thin films offer increased surface area which is favourable for light trapping due to a reduction in specular reflectance but increased internal scattering, leading to increased optical path lengths for photon absorption.
- In Photovoltaic thin film structures, transport lengths for photoexcited carriers in the absorber are reduced and so electrons and holes do not need to travel over large distances before separation and collection.

4.2.2 Thin -film deposition technique

The thin film deposition of photovoltaic materials takes place by electron beam, resistance heating and sputtering techniques. These technologies differ from each other in terms of degree of sophistication and quality of film produced. A resistance-heated evaporation technology is relatively simple and inexpensive, but the material capacity is very small which restricts its use for commercial production line. Sputtering technique can be used to deposit on large areas and complex surfaces. Electron beam evaporation is the most versatile technique of vacuum evaporation and deposition of pure elements, including most metals, numerous alloys and compounds. The electron beam technology has an edge over its counterparts due to following merits of this technology:

- precise control at low or high deposition rates is possible
- possibilities of co-deposition and sequential deposition systems are available
- uniform low temperature deposition is possible
- excellent material utilization is possible
- higher evaporation rates are possible
- freedom from contamination is possible
- precise film composition and cooler substrate temperatures can be maintained

4.2.2.1 e-Vap® thin film deposition technology

Various frames of different electron beam sizes are offered by e-Vap® which are able to produce small research specimen to achieve commercial coating requirement with crucible capacities from 2cc to 400cc. e-Vap® 100 miniature evaporation systems is a precise wire-fed electron beam source designed specifically for depositing monolayer thin films in ultrahigh vacuum environments capable to deposit metals at atomic level. e-Vap® 3000 and Caburn-MDC e-Vap® are other electron beam evaporation system of different capacity for a wide range of applications[30]. Various companies are working in the field of thin film photovoltaics as shown in Table 1.

Major companies	Technology	Status of manufacturing
Siemens Solar Industries (SSI), Global Solar	Copper Indium Diselenide	Initial Small Quantity Manufacture under 100 kW at SSI
First Solar, BP Solar, Matsushita	First Solar, BP Solar, Matsushita	First Solar Production under 1 MW, Others Lower
Solarex, United Solar, Canon, others	Amorphous Silicon	Commercial Production under 10 MW at Several Plants

Table 1. Photovoltaic thin film manufacturing

4.3 Printing of plastic solar cells

Organic semiconductor based solar cells can be integrated fast with textile substrates and molecular heterojunction cells can be printed using inkjet printing efficiently. This technology has opened new routes to produce organic solar cells. Credit of invention of printed solar cells goes to Konarka Technologies[31] for successful demonstration of manufacturing of solar cells by inkjet printing as shown in Fig.4 .

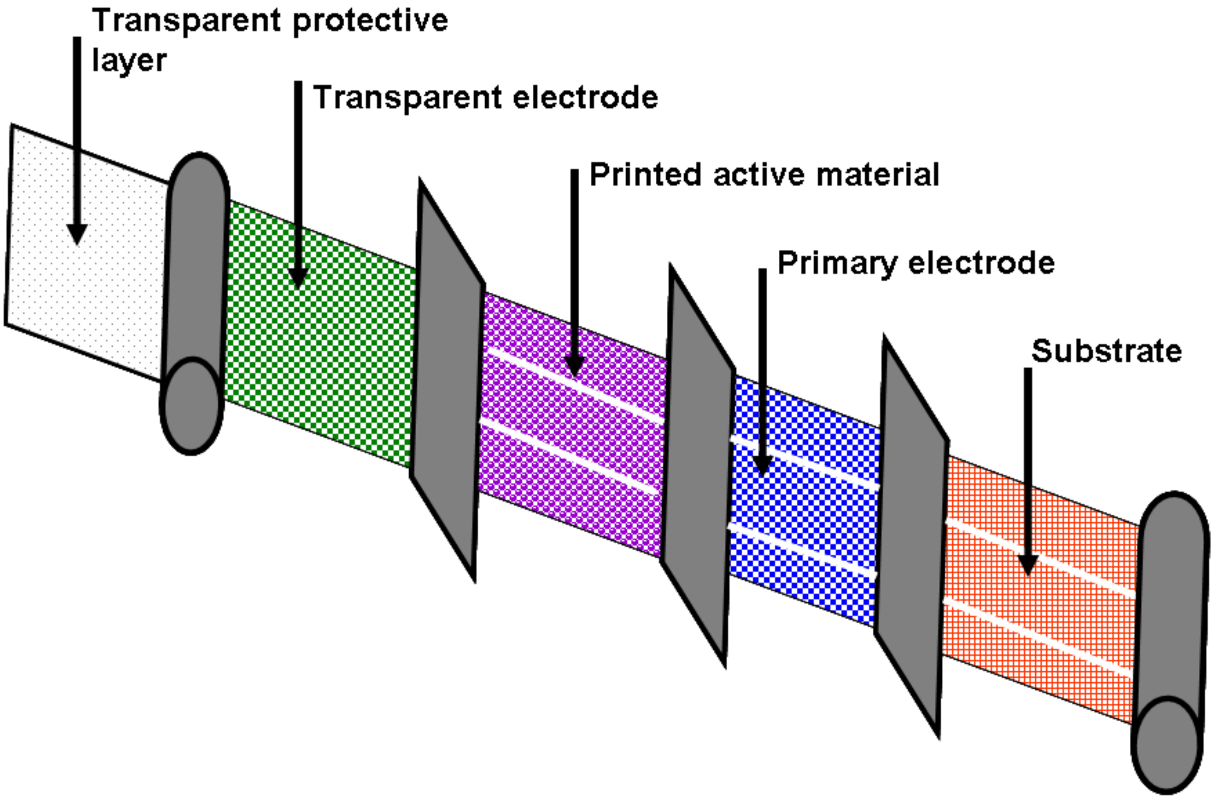

Fig. 4. Konarka’s plastic photovoltaic cells by printing technology

The inkjet printing technology enables manufacturing of solar cells with multiple colors and patterns for lower power requirement products, like indoor or sensor applications. A mixture of high and low boiling solvents, (68% orthodichlorobenzene and 32% 1,3,5-trimethylbenzene), is found suitable for the production of inkjet printed organic solar cells with power conversion efficiency upto 3%. During the drying process and subsequent annealing, the suggested oDCB–mesitylene solvent mixture leads to an optimum phase separation network of the polymer donor and fullerene acceptor and therefore strongly enhances the performance. During drying and subsequent heat-setting process, the recommended ortho-dichlorobenzene (oDCB)-mesitylene solvent mixture leads to an optimum phase separation of polymer donor and fullerene acceptor as suggested by Pagliaro et al., (2008)[32]. Solvents formulation and temperature of printing table are two prime parameters to control the spreading and wetting of liquid on substrate surface. Fig.4 shows a schematic representation of organic film formation by inkjet printing.

In a typical case, the photoactive formulation is formed by blending poly(3-hexylthiophene) (P3HT) with fullerene [6,6]-phenyl C61 butyric acid methyl ester (PCBM) in a tetralene and oDCB–mesitylene solvent mixture. A uniform film and reliable printing with respect to the spreading and film formation was performed by keeping the inkjet platen temperature 40°C. The combination of higher/lower boiling solvent mixture, oDCB–mesitylene, offers following advantages:

a. oDCB with b.p.¼180°C can be used to prevent nozzle clogging and provide a reliable jetting of the printhead
b. the second component, mesitylene, with lower boiling point of 165°C of the solvent mixture, with a lower surface tension, is used to achieve optimum wetting and spreading of the solution on the substrate. It has a higher vapor pressure of 1.86mm Hg at 20°C and a lower boiling point of 165°C compared to oDCB and tetralene. It increases the drying rate of the solvent mixture, which is a critical parameter to decide the morphology of PV prints.

According to Hoth et al., (2007) for an efficient bulk heterojunction solar cell, precise control of the morphology is essential. The active layer deposition tool strategy decides the morphology. It was evident from AFM study of the inkjet printed active layers that the P3HT–PCBM blend films show significant difference in the grain size and surface roughness. The roughness of active layer surface affects the performance of the inkjet printed photovoltaic device. The credit of commercialization of power plastic cells (PPC) goes to Konarka alongwith a German firm Leonhard Kurz by opting simple, energy efficient, environmentally friendly, replicable and scalable process. The semiconducting conjugated polymers to make the photosensitive layers of the cell are created in batches of several liters each. Finally fluffy powder is formed and manufacturers combine it with standard industrial solvents to create an ink or coatable liquid. This coatable liquid is fed in reservoir of inkjet print head. Specific types of pumps are used to exert continuous pressure to maintain constant through put rate from orifice inkjet printhead throughout the printing process. Inkjet head has facility to move in different directions which helps to create various printing patterns of semiconducting polymer liquid on textile substrate layer by layer as shown in Fig.5. These layers are considerably thin. During deposition of semiconducting polymer cleanliness is very important and whole printing process is carried out in a clean room[31].

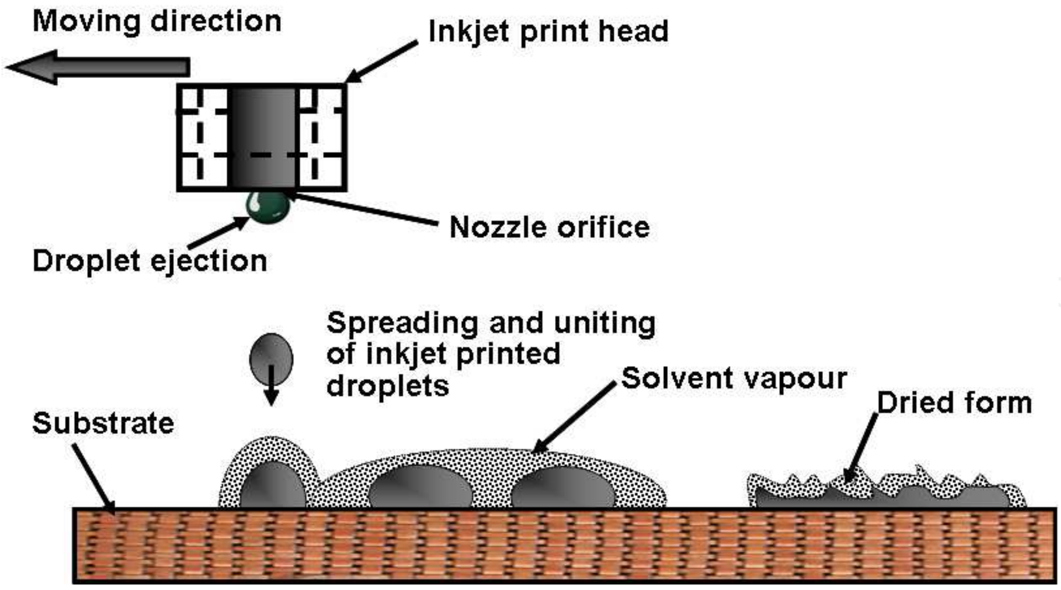

Fig. 5. Inkjet printing of photovoltaic cells

4.3.1 Advantages of inkjet printing

Inkjet printing of organic photovoltaic materials offers following advantages:

- Inkjet printing is a commonly used technique for controlled deposition of solutions of functional materials in specific locations on a substrate and can provide easy and fast deposition of polymer films over a large area.
- Organic solar cells can be processed with printing technologies with little or no loss compared to clean room, semiconductor technologies such as spin coating.
- Inkjet printing could become a smart tool to manufacturer solar cells with multiple colors and patterns for lower power requirement products, like indoor or sensor applications.
- Inkjet printing technique is considered very promising because the polymer devices can be fabricated very easily because of the compatibility with various substrates and it does not require additional patterning.

5. Significance of low bandgap polymers

The part of visible sunlight is lost by absorption in specific regions of the spectrum when passes through the atmosphere. The amount of loss depends on the air mass. Under ideal conditions, the available photons for the conversion to the electrons can be represented by the solar spectrum in photon flux as a function of wavelength. It is evident that photons must be harvest at longer wavelength but at longer wavelengths the energy of the charge carriers remains lower which restricts the voltage difference that the device can produce. Hence designing of optimum bandgap is essential. However, the practical efficiencies differ from theoretically predicted values. These above considerations are based on the fact that the low band gap polymers have the possibility to improve the efficiency of OPVs due to a better overlap with the solar spectrum. Hence to achieve maximum power generation in photovoltaic device low band gap materials are required. Majority of Photovoltaic devices are unable to convert light energy below 350–400 nm wavelengths efficiently into electrical energy because of poor absorption in the substrate and front electrodes. Although, this part of light spectrum contains very little intensity and consequently do not have a major contribution and i.e only 1.4% to the total possible current. It is evident from above discussion that to increase the current realization λ_{max} have to increase from 650 to 1000nm, in turn decreasing the band gap. Poly (3-hexylthiophene) is a typical example of low badgap polymeric material has a band gap of 650nm (1.9 eV) which can harvest up to 22.4% of the available photons. Hence, it is necessary to fabricate the polymers having broad absorption to achieve increase in the efficiency of the solar cell[33-34].

6. Different techniques to manufacture photovoltaic textiles

Photovoltaics and textiles are two different areas where a successful collaboration brings very smart results. The integration of these two different sectors can be possible by adopting following techniques.

There are two basic techniques to manufacture PV textiles.

6.1 PV textiles by PV fibres

This technique is based on the development of photovoltaic fibres using Si-based /organic semiconducting coating or incorporation of dye-sensitized cells (DSC). Availability of PV fibre offer more freedom in the selection of structure for various type of applications[35-39].

The development of photovoltaic fibres offers advantages to manufacture large area active surfaces and higher flexibility to weave or knit etc[40].

Although, the problem of manufacturing textile structure by using dye-sensitized cells (DSC-PV) fibres into textile structure is still alive and require a optimization with respect to textile manufacturing operations. In a typical research work the working electrode of DSC-PV fibre is prepared by coating Ti wire with a porous layer of TiO_2. This working electrode is embedded in an electrolyte with titanium counter electrode. The composite structure is coated with a transparent cladding to ensure protection and structural integrity. The electrons from dye molecules are excited by photo energy and penetrated into the conduction band of TiO_2 and move to the counter electrode through external circuit and regenerate the electrolyte by happening of redox reaction. Ultimately the electrolyte regenerates the dye by means of reduction reaction.

The performance of DSC fibre is majorily depends on the grade of TiO_2 coating and its integration to Ti substrate. The integrity of Ti with TiO_2 will depend on the surface cleanliness and roughness of Ti, affinity between Ti and TiO_2 and other defects. The deposition of TiO_2 dye on Ti wire surface is performed by strategy as shown in Fig.6. The integrity of coating on Ti substrate is tested by using peel test, tensile test, four point bending test and scratch test. The amount of discontinuities is measured by optional microscopy and SEM[41-47].

The photovoltaic potential of dye-sensitized solar cells (DSSC) of Poly(vinyl alcohol) (PVA) was improved by spun it into nanofibers by electrospinning technique using PVA solution containing silver nitrate ($AgNO_3$). The silver nanoparticles were generated in electrospun PVA nanofibers after irradiation with UV light of 310~380 nm wavelength. Electrospun PVA/Ag nanofibers have exhibited I_{sc}, FF, V_{oc}, and η showed the values of 11.9~12.5 mA/cm^2, 0.55~10.59, 0.70~10.71 V, and 4.73~14.99%, respectively. When the silver was loaded upto 1% as dope additives in PVA solution, the resultant electrospun PVA/Ag nanofibres exhibited power conversion efficiency 4.99%, which is higher than that of dye sensitized solar cells (DSSC) using electrospun PVA nanofibers without Ag nanoparticles[48].

Ramier et al., (2008), concluded that the feasibility of producing textile structure from DSC-PV fibre is quite good. The deposition of TiO_2 on flexible fibre is expected to be quite fruitful in order to maintain the structural integrity without comparing with PV performance[49].

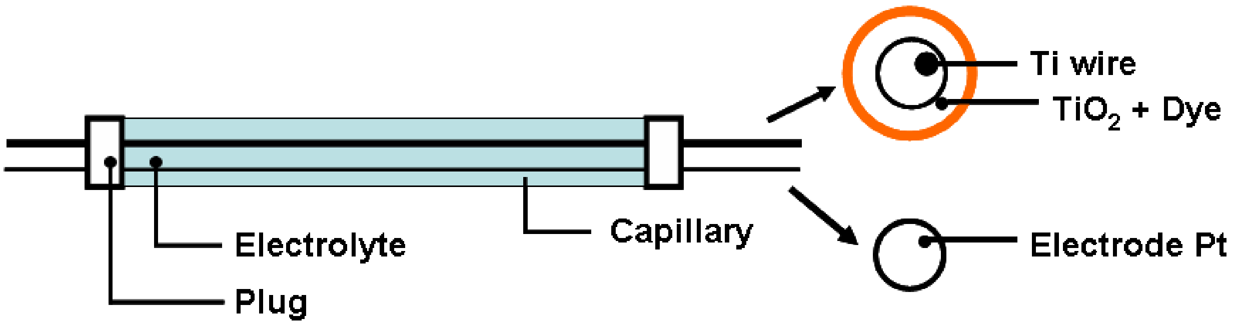

Fig. 6. A model DSC Photovoltaic fibre by surface deposition

Fibre based organic PV devices inroads their applications in electronics, lighting, sensing and thermoelectric harvesting. By successful patch up between commodity fibre and photovoltaic concept, a very useful and cost effective way of power harvesting is matured[50-52].

Coner et al.,[53] have developed a photovoltaic fibre by deposition of small Molecular weight organic compound in the form of concentric layer on long fibres. They manufactured the OPV fibre by vacuum thermal evaporation (VTE) of concentric thin films upto 0.48 mm thickness on polyamide coated silica fibre. Different control devices are based on OPV cells containing identical layer structures deposited on polyimide substrates. The OPV based fibre cells were defined by the shape of the substrate and 1 mm long cathodes. All fibre surfaces were cleaned well prior to deposition. Lastly, they concluded that performance of OPV fibre cells from ITO is inferior in terms of changes in illumination angle, enabling the optical photovoltaic (OPV) fibre containing devices to outperform its planar analog under favourable operating conditions. Light emitting devices are designed in such a way that becomes friendly to weave it. The light trapping on fibre surface can be improved by using external dielectric coating which is coupled with protective coating to enhance its service time. Successful PV fibre can be manufactured by opting appropriate material with more improved fabrication potential[54].

Dye sensitized solar cells (DSC) are low cost, applicable in wide range of application and simple to manufacture. These merits of dye-sensitized PV fibre makes it a potential alternative to the conventional silicon and thin film PV devices[55].

DSC works on the principle of optoelectronically active cladding on an optical fibre. This group was manufactured two type of PV fibre using polymethylmethacrylate (PMMA) baltronic quality diameter 1.3 to 2.0mm and photonium quality glass fibre with diameter 1.0 to 1.5 mm. Both virgin fibre were made electronically conductive by deposition of 130nm thick layer of ZnO:Al by atomic layer deposition technique with the help of P400 equipment. The high surface area photoelectric film for DSC was prepared in two steps. In first step TiO_2 in the form of solution or paste having TiO_2 nanoparticle is deposited on electronically conductive surface. In the second step dry layer of TiO_2 is sintered at 450-500°C for 30 minute to ensure proper adhesion to the fibre surface. PMMA fibre is suitable to survive upto 85°C. Hence mechanical compression is alternate technique to ensure the fixation.

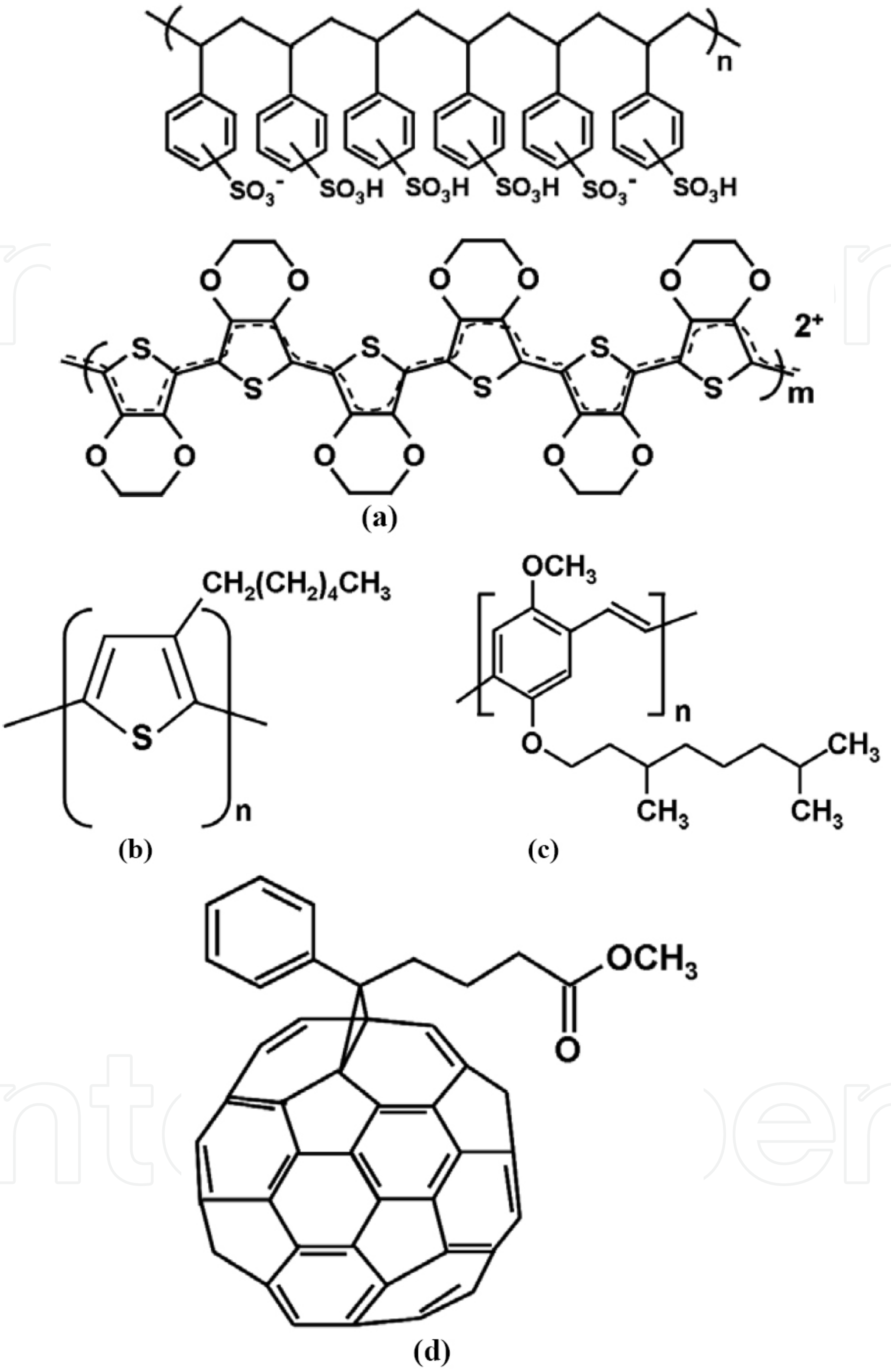

Fig. 7. Chemical configurations of (a) PEDOT:PSS (b) P3HT (c) MDMO-PPV (d) PCBM

Glass fibre is capable to withstand with sintering temperatures which inroads the possibilities of preparation of porous photoelectrodes on them. Commercially available TiO_2 paste was diluted to achieve appropriate viscosity with tarpin oil to make suitable for dip-coating. TiO_2

film was formed by dip coating and dried at room temperature upto 30 min before proper sintering between 475 to 500°C. Appropriately sintered fibres were then immersed in dye solution consisting of 0.32 ml of the cis-bis(isothiocyanate)bis(2,2-bipyridyl-4-4' dicarboxylato)-ruthenium(II) bis-tetrabutyl ammonium, Solaronix SA with trade name N719 dye in absolute ethanol for 48h. The dyeing of nonporous Polymethylmethacrylate (PMMA) fibre coated with nonporous TiO_2 layer was performed in the same dye bath. After complete senetization the excess dye was rinsed away with ethanol. A electrolyte solution was prepared with 0.5 M 4-tert butylpyridine and 0.5 M Lil, 0.05MI2 in 3 methoxypropionitrile (MePRN) with 5 wt% polyvinylidene fluoride-hexafluoro-propylene(PVDE-HFP) added as gelatinizing agent as used by Wang et al., (2004)[56].

Finally gelatinized iodine electrolyte was added next with dip coating from hot solution. Lastly the carbon based counter electrode was coated by means of a gel prepared by exhaustive grinding of 1.4g graphite powder and 0.49 grade carbon black simultaneously.

6.1.1 Manufacturing of photovoltaic fibres as per Bedeloglu et al.,[57-58] method

Bedeloglu et al., have used nontransparent PP as substrate. The PP tape was washed using methanol, isopropanol and water and then dried in N2 atmosphere. Thermal evaporation technique was used to deposit 100nm thick Ag contact layer on PP substrate. A filtered solution of PEDOT: PSS, chemical structure shown in Fig.7, in 5% dimethyl sulfoxide (DMSO) and stirred with 0.1% Triton X-100 to increase the thermal conductivity and cohesiveness properties. Stirred mixture of PEDOT: PSS were deposited on cleaned PP tapes at a thickness of 200 nm by dip coating technique. A blend of P3HT as conjugated polymer and PCBM was stirred upto 24h in chlorobenzene and then dip coated with thickness of 200 nm on top of PEDOT: PSS layer. Finishing of all PV structures was completed in vacuum chambers. An aluminium contact layer of approximately 3 nm thickness was deposited followed by 7nm thick Ag layer as anode. The purpose of Al layer was to avoid short circuiting between Ag and PEDOT: PSS films. The resultant photovoltaic fibre is shown in Fig.8.

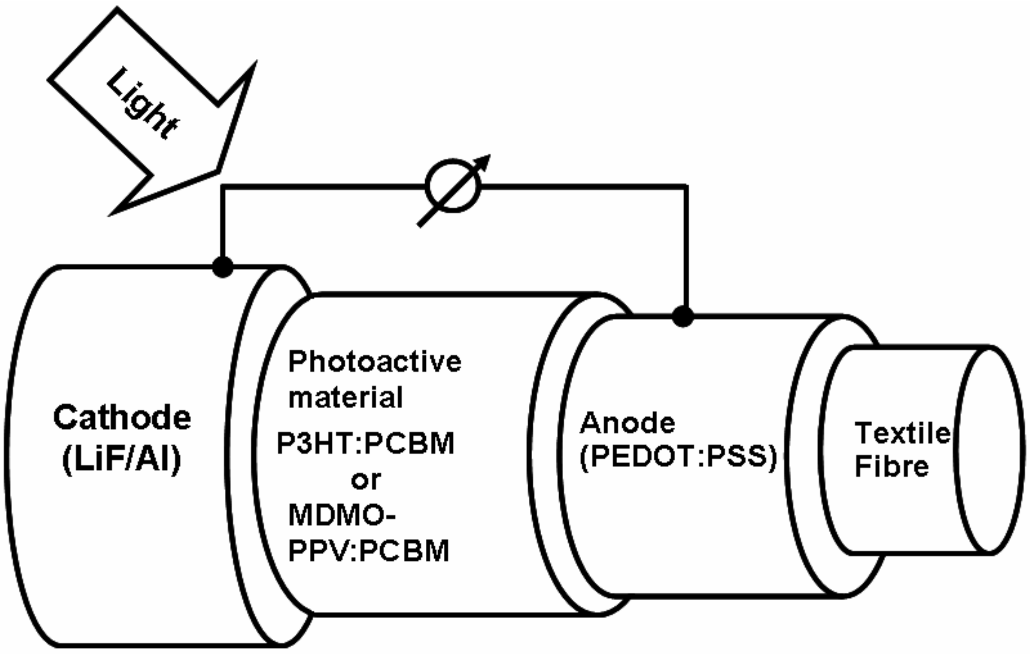

Fig. 8. Schematic representation of Photovoltaic fibre

A group of Turkish scientists has standardized a photovoltaic fibre manufacturing process. A monofilament supply cope is used to supply the basic filament for PV fibre manufacturing. This monofilament is cleaned in a bath by methanol solution and then further clean up by isopropanol solution in second bath. The cleaned fibre surface is washed with distill water followed by drying with dry nitrogen flow. The fibre is immersed in fourth bath containing mixture of PEDOT: PSS followed by oven drying at 50°C for 3 hr. The coated fibres are further immersed in another subsequent bath containing photoactive material solution and then dried out at 50°C for 15 min in oven. After drying, deposition of metal electrode takes place on fibre surface followed by deposition of anti-reflective materials by appropriate deposition technique. Finally a protective layer is laminated on fibre surface. In consequence of this process, a photovoltaic fibre is manufactured and become ready for power harvesting.

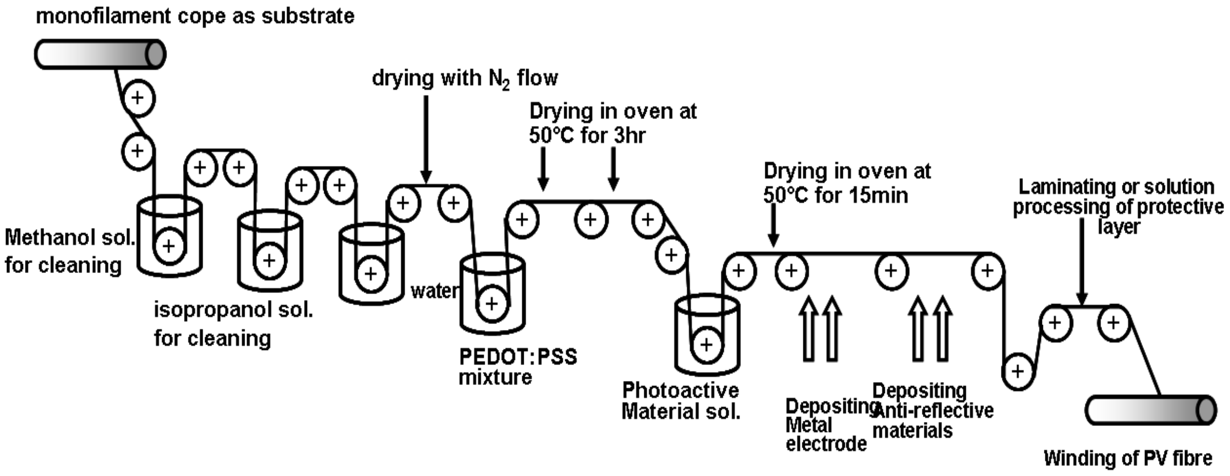

Fig. 9. Manufacturing process of Photovoltaic fibre as suggested by Bedeloglu et al.[21]

6.2 PV textiles by patching (attachment of PV cells to existing textile structures)

Under this technology a solar cell is manufactured separately and then patched onto textile structure by different ways. Thin film solar cells with adequate flexibility can be patched successfully on textile surfaces to impart PV effect. This technique is most appropriate to easily develop both small and large area structures with low cost, and light weight.

In a typical approach thin layers of polymer photovoltaics are laminated onto a textile substrate followed by plasma treatment and coating of PEDOT electrode. Subsequent screen printing of the active material and evaporation of the ultimate electrode finished the polymer photovoltaic that is fully integrated into the textile material[59].

Poly 1,4-(2-methoxy-5-(2-ethylhexyloxy))phenylenevinylene (MEH-PPV) was synthesized by polymerization of α,α′-dibromo-2-methoxy-5-(2-ethylhexyloxy) xylene as described by Neef and Ferraris. The purified MEH-PPV was characterized and found the Mw of 249,000 g mol^{-1} , polydispersity of 5.46 and a peak molecular weight Mp of 157,500 g mol^{-1}. A polyethylene terephthalate (PET) film of thickness 200 μm covered with 50 Ω^2 ITO layer was iched by 20% HCL and 5%HNO_3. A 250 μm thick polyethylene film was thermally laminated on polyethylene terephthalate (PET) surface. Both PET and PE surfaces was plasma treated using a 350-1 low power 3-phase AC plasma system as prescribed by Jensen and Glejbol (2003) in order to obtain optimum etching to get appropriate adherence with textile substrates[60-61].

Plasma treatment was followed by application of PEDOT electrode deformation by spray painting of an inhibited mixture of Iron (III) Tosylate and 3,4-Ethylene-dioxythiopene (EDT) through an aluminum mask. As the temperature reaches 50°C inhibitors are started to evaporate and polymerization of EDT initiated. After completing the polymerization, the PEDOT-coated textile was washed in cold water twice to washout excess tosylate, Iron (II) and inhibitor residuals and finally annealed in air at 50°C for 2 hour.

The materials that can generate electricity by photon conversion are loaded with fibres, yarns and textile structures inherently to offer PV effect.

Chlorobenzene was used to get the solution of MEH-PPV of 3.5gL^{-1}. The solution was filtered through a filter of 2.7μm filter and coated on polyethylene terephthalate- Indium tin oxide (PET-ITO) substrate by doctor blade coating system. Consequently a homogeneous red colour film is coated on PET-ITO substrate. Cholorobenezene solution of 25gL^{-1} was used to get printed pattern of polymer by means of screen-printing. The masks were prepared by using threads of 27 micron diameter with 140, 180,200 and 220 fibres cm^{-1} mesh. Finally, the printed substrates were dried in absence of sunlight. Photovoltaic device was prepared by following manner. The PET-ITO-MEHPPV substrates were incorporated behind a mask and a layer of C60 and aluminium was deposited by thermal evaporation technique. After completing the evaporation the device was laminated on 100 micron PET substrate on electrode side. The screen printed photovoltaic textile was mounted on large evaporator and kept the distance between thermal source and substrate 65 cm. The PV textile holder was rotated at 30 rpm. The aluminium electrodes were prepared in the form of 300 nm thick layers. The evaporation chamber was filled with dry nitrogen after completing the 30 min cooling. Electrodes were integrated with textile substrate by using silver epoxy[62].

7. Characterization of photovoltaic textiles

Characterization of various photovoltaic textiles is essential to prove its performance before send to the market. Various characterization techniques collectively ensures the perfect achievement of the targets to manufacture the desired product.

7.1 Thickness and morphology of photovoltaic textiles

Scanning electron microscope is used to investigate the thickness and morphology of various donor, acceptor layers. Scanning electron microscopes from LEO Supra 35 and others can be used to measure the existence and thickness of various coated layers on various textile surfaces at nanometer level. Various layers on photovoltaic fibres become clearly visible with 50000X magnification. The thickness of the layers can be seen from SEM photographs by bright interface line between the polymer anode and the photoactive layer.

7.2 Current and voltage

In order to characterize the Photovoltaic fibres open circuit voltage, short circuit current density, current and voltage at the maximum power point under an illumination of 100 mW/cm^2 are carried out.

In order to calculate the Photovoltaic efficiency of Photovoltaic textiles, current verses voltage study is essential. To achieve this target a computer controlled sourcemeter equipped with a solar simulator under a range of illumination power is required with proper calibration. All photoelectrical characterizations are advised to conduct under nitrogen or argon atmosphere inside a glove box to maintain the preciseness of observations. The overall efficiency of the PV devices can be representing by following equation.

$$\eta = \frac{V_{oc} \times I_{sc} \times FF}{P_{in}} = \frac{P_{out}}{P_{in}} \tag{1}$$

Where

V_{oc} is the open circuit voltage (for l=0) typically measured in volt (V)

I_{sc} is the short circuit current density (for V=0) in ampere /square meter (A/m^2)

P_{out} is the output electrical power of the device under illumination

P_{in} the incident solar radiation in (watt/meter^2) W/m^2

FF is the fill factor and can be explained by the following relationship:

$$FF = \frac{I_{mpp} \times V_{mpp}}{I_{sc} \times V_{oc}} \tag{2}$$

where,

V_{mpp} voltage at the maximum power point (MPP)

I_{mpp} is the current at the maximum power point (MPP)

Where the product of the voltage and current is maximized

To assure an objective measurement for precise comparison of various photovoltaic devices, characterization has to be performed under identical conditions.

An European research group has used Keithley 236 source measure unit in dark simulated AM 1.5 global solar conditions at an intensity of 100mW cm^{-2}. The solar simulator unit made by K.H. Steuernagel Lichttechnik GmbH was calibrated with the help of standard crystalline silicon diode. PV fibres were illuminated through the cathode side and I-V characteristics were measured. The semi-logarithmic I-V curves demonstrate the current density versus voltage behaviour of photovoltaic fibres under various conditions. It gives a comparative picture of voltage Vs current density as a function of various light intensities.

Durisch et al., (1996) has developed a computer based testing instrument to measure the performance of solar cells under actual outdoor conditions. This testing system consist a suntracked specimen holder, digital multimeters, devices to apply different electronic loads and a computer based laser printer. Pyranometers, pyrheliometers and a reference cell is used to measure and record the insulation. This instrument is able to test wide dimensions of photovoltaic articles ranging from 3mm X 3mm to 1 meter X 1.5meter. The major part of world's energy scientist community predicts that photovoltaic energy will play a decisive role in any sustainable energy future[63].

7.3 Electroluminescence

The institute for Solar Energy Research Hameln (ISFH) Emmerthal Germany introduced a new technique to characterize the solar cells based on electroluminescence. Electroluminescence can be defined as the emission of light resulting from a forward bias voltage application to the solar cells. The electrons recombine radioactively which are injected into the solar cells by transferring their extra energy to an emitted photon with available holes. The consequence of the electron and hole concentration is able to represent the intensity of the luminescence radiation. A powerful charge coupled device (CCD) camera is used to capture the images of intensity distribution of the luminescence radiation. Generally, actual solar cells offer inhomogeneous electroluminescence images but for an ideal solar cell it must be homogeneous. A cooled 12 CCD camera is used to capture electroluminescence images. The flexibility to adjust the distance between the camera and the solar cells offers the potential to analyse wide variety of solar cells.

7.4 Fill factor

The quality of solar cells is measured in terms of fill factor. The fill factor for a ideal solar cell is one but as internal resistance of solar cell becomes large or bad contact becomes between layers, fill factor reduces. The fill factor of textile based photovoltaics remains low due to bad quality of electrodes and/or poor contact between different layers of materials[64].

It can be improved towards unit by selection of appropriate textile substrate and further optimization process parameters and processes.

7.5 Mechanical characterization

Textile substrates are subjected to different stresses under various situations. Hence usual tensile characterization is essential for photovoltaic textiles. For tensile testing of PV fibres, the constant rate of extension (CRE) based tensile testing machines are used at 1 mm per minute deformation rate using Linear Variable Differential Transformers (LVDT) displacement sensor. Fracture phenomenon is recorded by means of high resolution video camera integrated with tensile testers.

To study about the adhesion and crack formation in coating on textile structures, generally 30 mm gauge length is used in case of photovoltaic fibres. Fibre strength measuring tensile tester, integrated with an appropriate optical microscope to record the images of specimen at an acquisition rate of about one frame per second is used to record the dynamic fracture of PV fibres. Different softwares are available to analyse the image data like PAXit, Clemex, and Digimizer etc.

7.6 Absorption spectra of solid films

Various spectrophotometers like Varian Carry 3G UV-Visible were used to observe the ultraviolet visible absorption spectra of photovoltaic films. The thin films are prepared to study the absorption spectrum of solid films. In a typical study, a thin film was prepared by spin coating of solution containing 10 mg of P3HT and 8mg of PCBM and 4.5 mg of MDMO-PPV and 18 mg of PCBM (in case of 1:4)/ml with chlorobenzene as solvent. A typical absorption spectra of MDMO-PPV:PCBM and P3HT: PCBM is illustrated in Fig 10.

7.7 X-ray diffraction of photovoltaic structures

Crystallization process is very common phenomenon that takes place during photovoltaic structure development. The content of crystalline and amorphous regions in photovoltaic structures influences the photoactivity of photovoltaic structures. X-ray diffraction technique is capable to characterize the amount of total crystallinity, crystal size and crystalline orientation in photovoltaic structures.

Presently, thin film photovoltaics are highly efficient devices being developed in different crystallographic forms: epitaxial, microcrystalline, polycrystalline, or amorphous. Critical structural and microstructural parameters of these thin film photovoltaics are directly related to the photovoltaic performance. Various X-ray techniques like x-ray diffraction for phase identification, texture analysis, high-resolution x-ray diffraction, diffuse scattering, x-ray reflectivity are used to study the fine structure of photovoltaic devices[65].

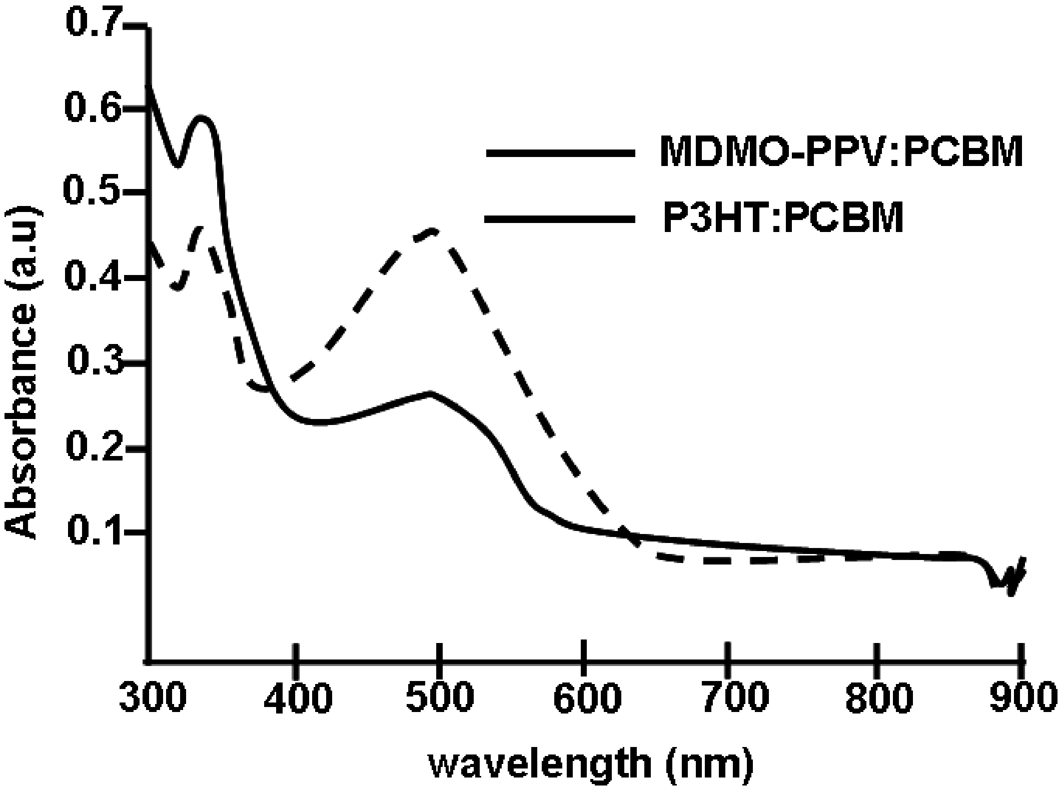

Fig. 10. Absorption spectra[57] for solutions of P3HTPCBM and MDMO-PPV-PCBM (with permission)

7.8 Raman spectroscopy

The Raman Effect takes place when light rays incidents upon a molecule and interact with the electron cloud and the bonds of that molecule. Spontaneous Raman effect is a form of scattering when a photon excites the molecule from the ground state to a virtual energy state. When the molecule relaxes it emits a photon and it returns to a different rotational or vibrational state.

Raman spectroscopy is majorly used to confirm the chemical bonds and symmetry of molecules. It provides a fingerprint to identify the molecules. The fingerprint region for organic molecules remains in the (wavenumber) range of 500–2000 cm^{-1}. Spontaneous Raman spectroscopy is used to characterize superconducting gap excitations and low frequency excitations of the solids. Raman scattering by anisotropic crystal offers information related to crystal orientation. The polarization of the Raman scattered light with respect to the crystal and the polarization of the laser light can be used to explore the degree of orientation of crystals[66].

The in situ morphological and optoelectronic changes in various photovoltaic materials can be observed by observing the changes in the Raman and photoluminescence (PL) feature with the help of a spectrometer. Various spectrums can be recorded at a definite integration time after avoiding any possibility of laser soaking of the sample[67].

8. Some facts about the photovoltaic textiles

- To achieve a highly efficient photovoltaic device, solar radiation needs to be efficiently absorbed. In case of solar cell the absorption of light causes electron hole pairs which are split into free carriers at the interface between the donor and the acceptor material.
- Active areas for photovoltaic fibres are generally found between 4 and 10mm^2.
- The power conversion efficiency of the MDMO-PPV:PCBM based photovoltaic fibre was higher than the P3HT:PCBM based photovoltaic fibres
- Due to circular cross-sectional shape of photovoltaic fibres, the light is absorbed at different angles
- Generally the photoactive layer thickness remain approximately between 280-350nm. A thick film can absorb more light compared to a thin film. By the increase of film thickness, the electrical field and the number of charge carriers decrease and consequently a decrease in the external quantum efficiency of the devices is observed. Although, the film thickness is restricted in presence of low-charge carrier. The optimum thickness is required to provide both maximum light absorption and maximum charge collection at the same fraction of moment. Optimization of thickness of various layers of photovoltaic fibres provides the possibility to increase the power conversion efficiency of polymer-based solar cells.
- The thickness of the layers for optimal photovoltaic fibre can be controlled by solution concentration and dipping time.
- Photovoltaic fibre based organic solar cells can be curled and crimped without losing any photovoltaic performance from their structure.
- Low power conversion efficiency of photovoltaic textiles is the real challenge in this field and can be improved by significant improvement in existing photovoltaic material and techniques. In case of organic solar cells, the optical band gap is very critical and it must be as narrow as possible because the polymers with narrow band gap are able to absorb more light at longer wavelengths, such as infrared and near-infrared. Hence low band gap polymers (<1.8 eV) can be used as better alternative for higher power harvesting efficiency in future if they are sufficiently flexible[68,69].
- The incorporation of C60 barrier layer can improve the performance of photovoltaic textiles.
- Generally the performance of freshly made photovoltaic textiles was found best because cell degradation happens fast when sun illumination takes place in absence of O_2 barriers.
- The self life of polymer based photovoltaics is short under ambient conditions[70].

9. Photovoltaic textile, developments at international level

The incorporation of polymer photovoltaics into textiles was demonstrated by Krebs et a., (2006) by two different strategies. Simple incorporation of a polyethyleneterphthalate (PET) substrate carrying the polymer photovoltaic device prepared by a doctor blade technique necessitated the use of the photovoltaic device as a structural element[71].

The total area of the device on PET was typically much smaller than the active area due to decorative design of aluminium electrode. Elaborate integration of the photovoltaic device into the textile material involved the lamination of a polyethylene (PE) film onto a suitably transparent textile material that was used as substrate. Plasma treatment of PE-surface allowed the application of a PEDOT electrode that exhibited good adherence. Screen printing of a designed pattern of poly 1,4-(2-methoxy-5-(2-ethylhexyloxy) phenylenevinylene (MEH-PPV) from chlorobenzene solution and final evaporation of an aluminum electrode completed the manufacturing of power generating device. The total area of the textile device was 1000 cm^2 (25cm x 40cm) while the active area (190 cm^2) was considerably smaller due to the decorative choice of the active material.

Konarka Inc. Lowell, Mass., U.S.A demonstrated a successful photovoltaic fiber. Presently, a German company is engaged with Ecole Polytechnique Fédérale de Lausanne (EPFL) to optimize the fiber properties and weave it into the power-generating fabric. Solar textiles would able to generate renewable power generation capabilities. The photovoltaic fibres are able to woven in fabric form rather than attached or applied on other surfaces where integration remains always susceptible. The structures woven by photovoltaic fibres are able to covert into fabric, coverings, tents and garments.

Patterned photovoltaic polymer solar cells can be incorporated on PET clothing by sewing through the polymer solar cell foil using an ordinary sewing machine. Connections between cells were made with copper wire that could also be sewn into the garment. The solar cells were incorporated into a dress and a belt as shown in Fig.11 (Tine Hertz).

Fig. 11. Textile solar cell pattern designed by Tine Hertz and Maria Langberg of Danmarks Designkole

Shafarman et al., (2003) demonstrated thin film solar cells by using CuInGaSe$_2$ photovoltaic polymers and this film is more suitable for patching onto clothing into different patterns[72]. The polymer photovoltaics technology is in its infancy stage and many gaps need to be bridged before commercialization. Prototype printing machines are useful to apply PVs on textile surface into decorative pattern as shown in Fig. 11, 12,13.

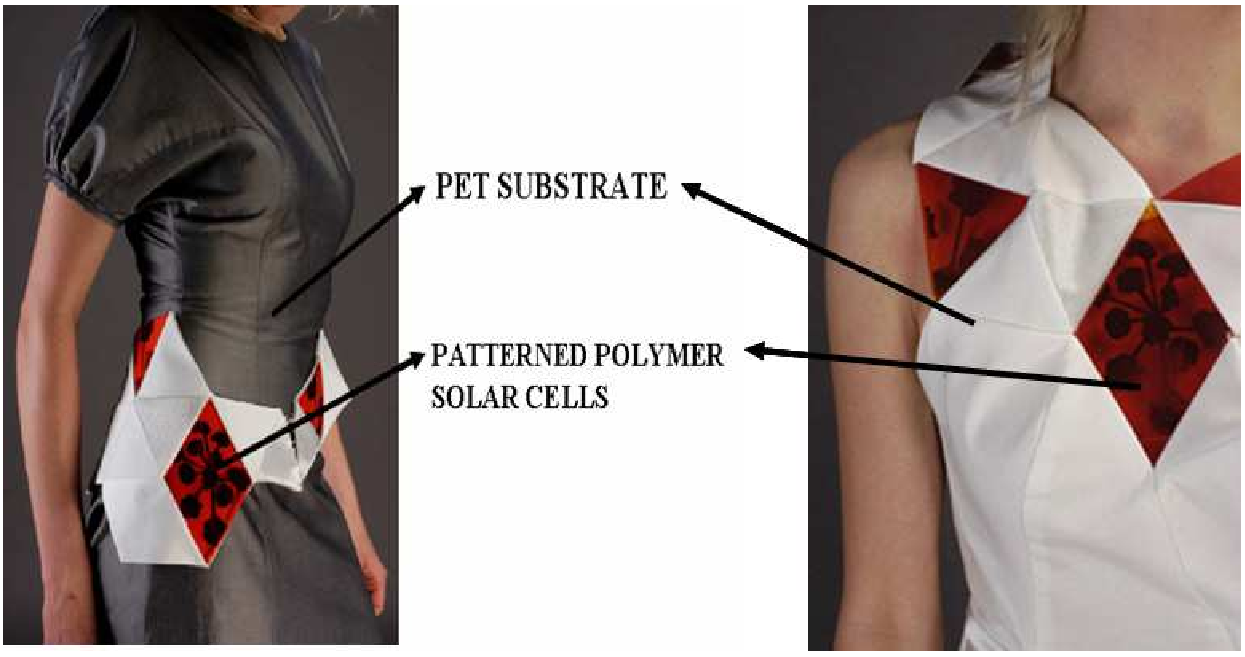

Fig. 12. Patterned polymer cell (with permission)

Fig. 13. Photovoltaic decorative patterns

Massachusetts Institute of Technology (MIT) Cambridge, Massachusetts revealed that the integration of solar cell technology in architecture creates designs for flexible photovoltaic materials that may change the way buildings receive and distribute energy. Sheila Kennedy of (MIT) used 3-D modeling software for her solar textiles designs, generating membrane-like surfaces that can become energy-efficient cladding for roofs or walls[73]. Solar textiles may also be used like tents as shown in Fig. 14.

Fig. 14. Photovoltaic textile as a tent (with permission)

Fig. 15. A typical example of photovoltaic textile (with permission)

- Commission for Technology and Innovation (CTI) Switzerland also exhibited a keen interest in the development of photovoltaic textiles.
- Thuringian Institute of Textiles and Plastics Research (TITK) registered their remarkable presence in order to develop photovoltaic textiles[74].
- J Wilson and R Mather have created Power Textiles Ltd, a spin-off from Heriot-Watt University, Scotland to develop a process for the direct integration of solar cells on textiles.
- Konarka is developing solar photovoltaic fabric with joint effort of the university Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland. Konarka has claimed that

they can produce a photovoltaic fiber. Presently, the Company is working with EPFL to optimize the fiber structure and weave it into the first power-generating fabric. Solar textiles would open up additional application areas for photovoltaics since renewable power generation capabilities can be tightly integrated

- In 2002, Konarka became the first company in the United States to license Dr. Michael Grätzel's dye-sensitized solar cell technology, which augmented its own intellectual property.
- Thuringian Institute of Textiles and Plastics Research (TITK), Breitscheidstraße Rudolstadt Germany, is a technically-oriented research institute, carrying out fundamental and applied research on PV textiles suitable to easily commercialize. The institute supports small and medium-sized enterprises in their innovation works with interdisciplinary scientific knowledge, innovative ideas, and knowledge of the industry and provision of modern technical infrastructure.
- Professor John Wilson and Dr Robert Mather of School of Textiles and Design, formerly the Scottish College of Textiles have created Power Textiles Ltd, a spin-off from Heriot-Watt University, to develop a process for the direct integration of solar cells on textiles.
- In a research work at American Institute of Physics, multiwall carbon nanotubes are introduced into poly(3-hexylthiophene) and [6,6] phenyl C_{61} butyric acid methyl fullerene, bulk heterojunction organic photovoltaic devices after appropriate chemical modification for compatibility with solution processable photovoltaics. To overcome the problem of heterogeneous dispersion of carbon nanotubes in organic solvents, multiwall CNT are functionalized by acid treatment. Pristine and acid treated multiwall carbon nanotubes have been incorporated into the active layer of photovoltaic polymers which results a fill factor of 0.62 and power harvesting efficiency of 2.3% under Air Mass 1.5 Global[75].
- Dephotex is going to develop photovoltaic textiles based on novel fibre under collaboration with European Union.
- Photovoltaic tents are developed by integration of flexible solar panels made by thin film technology by patching on tent fabric surface. The solar cells can run ventilation systems, lighting and other critical electrical functions, avoiding the need for both generators and the fuel to run them.

The integration of photovoltaic technology with UV absorption technology will open very smart passages to new product development. However, the above opinion is only a hypothesis of author. The textile materials which are stable against ultraviolet rays are more suitable to work as basic substrate. However, the production and integration of photovoltaic fibres into fabric form will solve many problems concerned about simple incorporation of a polymer photovoltaic on a textile substrate directly or by lamination of a thin layer of PVs onto textile material followed by plasma treatment and application of a PEDOT electrode onto the textile materials.

10. Conclusions

The incorporation of polymeric photovoltaics into garments and textiles have been explored new inroads for potential use in ''intelligent clothing'' in more smart ways. Incorporation of organic solar cells into textiles has been realized encouraging performances. Stability issues need to be solved before commercialization of various photovoltaic textile manufacturing techniques. The functionality of the photovoltaic textiles does not limited by mechanical stability of photovoltaics. Polymer-based solar cell materials and manufacturing techniques are suitable and applicable for flexible and non-transparent textiles, especially tapes and fibers, with transparent outer electrodes.

The manufactured photovoltaic fibres may also be utilized to manufacture functional yarns by spinning and then fabric by weaving and knitting. Fibres and yarns subjected to various mechanical stresses during spinning, weaving and knitting may possibly damage the coating layers of photovoltaic fibres. These sensitive and delicate structures must be protected by applying special protective layers by noble coating techniques to produce photovoltaic textiles. Photovoltaic tents, curtains, tarpaulins and roofing are available to utilize the solar power to generate electricity in more green and clean fashion.

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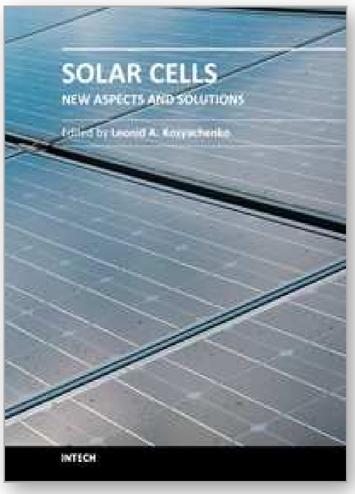

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The fourth book of the four-volume edition of 'Solar cells' consists chapters that are general in nature and not related specifically to the so-called photovoltaic generations, novel scientific ideas and technical solutions, which has not properly approved. General issues of the efficiency of solar cell and through hydrogen production in photoelectrochemical solar cell are discussed. Considerable attention is paid to the quantum-size effects in solar cells both in general and on specific examples of super-lattices, quantum dots, etc. New materials, such as cuprous oxide as an active material for solar cells, AlSb for use as an absorber layer in p-i-n junction solar cells, InGaAsN as a promising material for multi-junction tandem solar cells, InP in solar cells with MIS structures are discussed. Several chapters are devoted to the analysis of both status and perspective of organic photovoltaics such as polymer/fullerene solar cells, poly(p-phenylene-vinylene) derivatives, photovoltaic textiles, photovoltaic fibers, etc.

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