Efficiency of thin film photovoltaic paint: A brief review

Shaheer A Khan, Ataur Rahman

Abstract: ***The integration of thin film solar paint in the field of photovoltaics has received much attention because of its potential to replace the conventional solar cells. The solar paint has shown enormous potential due to its tunable size characteristics, flexibility and cost-effective way of manufacturing. However, there is still a need for the improvement in the power conversion efficiencies of these paints, which emphasis this study to do further for characterizing the optimum materials for the paint. The aim of this study is to find the materials for the paint from reviewing the related published materials, which would have high electrical and thermal conductivities. This study also focuses on the techniques to improve the solar power conversion efficiency by using the paint just applying on any conductive surface. The manuscript presents the recent developments of materials and synthesis techniques for developing photovoltaic paints. Consequently, it describes the suitable material and deposition technique to improve the efficiency of thin film photovoltaic paint.***

Keywords: Efficiency of solar paint; Nano-crystal ink; Spray-on thin film; Solution processed solar cell; Solar paint; Thin film.

I. INTRODUCTION

Renewable Energy or Clean Energy is increasingly becoming a vital factor as a substitute to traditional routes of generating electricity. This area has been adopted because of the rapidly changing environmental conditions, which are badly affecting the natural existence of gas, water, oil and coal [1]. For the past few years, there has been a rapid rise in the use of a type of renewable energy i.e. solar energy. It is widely used in commercial and non-commercial applications with many significant results.

Photovoltaic can be defined as the direct conversion of light energy into electrical energy and the devices, which perform this conversion are called photovoltaic devices [2]. At present, the photovoltaics are categorized into three generations. The first-generation photovoltaic consists of Crystalline Silicon (C-Si) solar cell having single p-n junction with the highest practical cell size conversion efficiencies. The second-generation photovoltaic consists of solar cells of CIGS (Copper Indium Gallium Celenide), CdTe (Cadmium telluride) and silicon in various forms i.e. (Amorphous, micro-crystalline and poly-crystalline) usually written as (a-Si, mc-Si, p-Si). The third-generation photovoltaics developed over the last decade consist of Dye-sensitized, Organic, Perovskite and Quantum dot solar cells [3]. Photovoltaic devices made up of crystalline solar cell have become an important material for commercial use due to its high-power conversion efficiency. The highest practical cell size efficiency of crystalline silicon solar cell achieved is 26.7% [4]. However, they have some limitations like limited number of cells (effects PCE), low light absorption coefficient due to indirect band gap, inflexibility and typical manufacturing process. On the other hand, solar paints are more appealing because these are light weight, few nanometers in size and flexible as compared to single crystal silicon wafer solar cells which are relatively big in size, bulky and breakable. Due to the existence of these paints in solution form, it also removes the barrier of installing limited number of solar cells in a confined area for the generation of electricity [5]. Furthermore, it can be applied to a large number of conductive surfaces including glass and plastic. Despite all these attractive features of photovoltaic paints, there is still a need to explore the ways to enhance the efficiency of these paints to make them effective for wide range of commercial applications [6].

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II. LITERATURE REVIEW

The papers included in this brief review are search using keywords “Solar Paint”, “Photovoltaic Paint”, “Solution processed nanocrystals”, and “Nanocrystal ink” from the databases. The selected literature is divided into five sections where in section 2.1, a brief description of solar paint is presented. The parameters governing the efficiency of photovoltaic paints are defined in second section. The third section provides a brief overview of materials used for making photovoltaic paints. In the fourth section different synthesis techniques are discussed and finally some reported efficiencies of solar paints are mentioned.

2.1. Solar paint

Solar Paint or Photovoltaic Paint terms appeared in the field of solar technology since 2005. There are many different terms available for defining Photovoltaic Paint such as Nanocrystal ink [7], Nanocrystal Photovoltaics, Spray on thin film PV and Quantum dot solar paint [7-9]. Solar paints are basically a class of thin film technology in which it can be fabricated in the form of solution. This solution is applied on glass or plastic substrate by spraying or brushing to make a complete solar cell. Some of the most attractive features of PV paints are thin layer deposition, substrate availability, less waste during processing and infragility. Second and third generation photovoltaic materials are used for making photovoltaics paints which are based on hybrids, organic and inorganic semiconductors including the nanostructured solar cell. All nano materials cannot be prepared in the form of solutions but some layers

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of organic, dye-sensitized, and quantum dots thin film solar cells can be processed in solution form A typical schematic of photovoltaic paint is shown in Figure 1 [10].

Sunlight

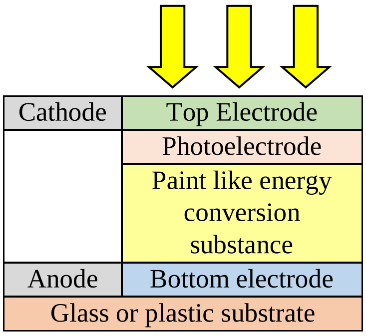

Fig. 1: Schematic diagram of thin film photovoltaic paint.

The working principle of photovoltaic paint with a thin film architecture can be described as when sunlight strikes the light absorbing material (photoelectrode), electrons of photoelectrode gains energy and a high-energy electron drifts into a layer of paint like substance, leaving behind an electron vacancy. Transparent top electrode collected the electron and power is generated using the energy from the electron. This used electron moves to the bottom electrode and complete the circuit by combining with an electron vacancy as illustrated in Figure 1. The solar paint also has the potential to combine the sensitizer and large bandgap semiconductor in a single layer [11].

2.2. Parameters affecting the efficiency

Power conversion of solar cells is based on the principle of photovoltaic effect. Photons of energies greater than the band gap energy (E_g) are absorbed and as a result, an electron excites from the valence band to conduction band. Solar cells have inbuilt asymmetry which causes the electrons to reach towards external circuit using an electrical potential. For achieving better efficiency, simultaneous enhancement of Open circuit voltage (Voc), Short circuit current density (Jsc) and fill factor (FF) are required.

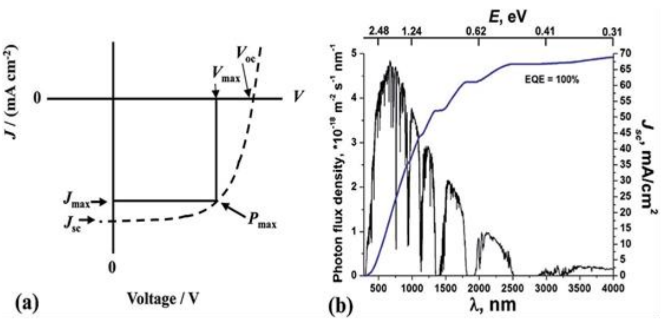

Fig.2: (a) Current density vs voltage for a solar cell; (b) Photon flux density and maximum attainable short circuit current density.

The parameters that affect the power conversion efficiency (PCE) can be expressed [12]:

$$PCE = \frac{J_{sc} V_{oc} FF}{P_{polar}} \quad (1)$$

where,

V_{OC} : Open circuit voltage, J_{SC}: Short circuit (photo) current, FF: Fill factor (It is a ratio of $P_{max} = J_{max} V_{max}$ and is defined as the product of J_{SC} and V_{OC} and is also a measure of the squareness of J vs V profile).

Efficiently extracting the photogenerated electrons and holes is a key parameter towards highly efficient solar cells. Solar cell performance is determined by the measurement of current density as the potential across the photovoltaic device is biased with the variable load during the irradiation of device by light as shown in Figure 2(a).

As the energy of photon is inversely proportional to the wavelength 1240/λ[nm]); Therefore, the value of short circuit photo current (J_{SC}) depends on the value of bandgap energy E_g . If the value of E is greater than the value of E_g and the solar spectrum is over the visible and infra-red regions, then generally the J_{SC} factor increases with the increasing λ as shown in Figure 2(b) [24]. Even though power conversion efficiency (PCE) increases with J_{SC}, there is also an existence of optimum value of E_g for attaining significant PCE because of the trade-off associated with V_{OC}. The bandgap energy (E_g) required achieving optimum power conversion efficiency ranges from 1.0 to 1.6 eV for the crystalline silicon solar cell. However, photovoltaic paint requires bandgap energy (Eg) ranging from 0.6 to 1.1 eV to achieve optimum power conversion efficiency through utilizing multiple exciton generation. There is an exponential decrease in the absorption of light intensity with the increase in film thickness [13]. Therefore, thickness of the photoactive layer is a vital factor dominating the PCE for a solar cell as compared to the absorption length (1/α), where "α" is the absorption coefficient in cm^{-1} and it is the distance over which 63% of the non-reflected light is absorbed. Crystalline solar cells have relatively low values of α, which results in the need of thicker photoactive layers of hundreds of millimeters and micrometers and this significantly cause an increase in the production cost of crystalline solar cells. Conversely, photovoltaic paints need thinner photoactive layers, which in turns result in the reduction of production and material costs.

2.3. Materials for photovoltaic paint

First-generation materials lack sufficient ability to be shaped as a liquid solar cell (a desired property required for making solar paints). Therefore, Second and third generation solar cell materials are used in the making of photovoltaic paints.

Second-generation materials are the first thin film photovoltaics consists of amorphous and polycrystalline materials. These materials offer thick deposition layer, large surface area and uses expensive toxic material, which results in its inadequate performance as compared to the first-generation materials. Therefore, there is a need arises to move towards third generation cells. Currently, third generation cells are still in research as compared to the other generation's cells, which were commercialized. Photovoltaic devices made up of third generation solar cells are lagging in efficiency as compared to its counterpart. However, the photovoltaics of third generation offers unique characteristics which differs it from the previous generations

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in few aspects: Third generation solar cells are based on thin-films of organic polymers, organic dyes and inorganic layers deposited on conductive substrates or as quantum dot nanocrystals embedded in a matrix using a "bottom-up" approach. On the contrary, first generation solar cells are based on wafer technology in which a bulk material usually silicon cuts into wafers using a "top-down" approach. Moreover, third generation cells are less dependent on conventional single p-n junction configuration for the segregation of photo-generated carriers. Rather, tandem cell consists of multiple p-n junctions are usually used in third generation cell for this purpose. Ultimately, this offers coverage of wide range of solar spectrum due to its infinite stack of a cascade with numerous band gaps (E_g). A brief description of the power conversion efficiencies of all three-generation solar cells is shown in Table 1.

III. RESULTS

Table 1: Best Research Cell efficiencies of different generation solar cell

Generation	Solar Cell Type	Efficiency (%)	Reference
First	Crystalline Silicon	26.7 ± 0.5	[14]
First	Multi Crystalline Silicon	22.3 ± 0.4	[15]
Second	Amorphous Silicon	14.0 ± 0.4	[16]
Second	Micro Crystalline Silicon	11.9 ± 0.3	[17]
Second	CIGS (cell)	23.3 ± 1.2	[18]
Second	CdTe (thin film)	22.1 ± 0.5	[19]
Third	Dye sensitized (cell)	11.9 ± 0.4	[20]
Third	Organic (thin film)	11.2 ± 0.3	[21]
Third	Perovskite (thin film)	22.7 ± 0.8	[22]
Third	Quantum dot sensitized	9.56 ± 0.12	[23]

The third generation solar cells are lagging to achieve the level of efficiency comparable with other generations (Table 1). Therefore, the selection of materials for photovoltaic paint is a critical factor towards the enhancement of efficiency. Each material has its own attractive features. However, the selection of each material associates with the availability of raw materials and adequate manufacturing process. Most of the second and third generation materials satisfies the criteria of making photovoltaic paint. The desired requirement of material for photovoltaic paint is highlighted in Table 2 [24-25].

Among the different architectures of materials, Tandem solar cell incorporated with Quantum dot solar cell (QDSSC) has tunable band-gap, which varies by changing their size. Conversely, the choice of material makes the bandgap fixed in bulk materials (CIGS or CdTe) [26]. Moreover, QDSSC has higher absorption coefficient, tunable bandgap, ability to generate multiple electron-hole pair just after striking with one photon, large size confinement, higher doping capabilities and possess synthesis technique without the requirement of high temperature and vacuum [27]. These properties give QDSSC edge over dye-sensitized solar cell and make it a potential candidate for the efficiency enhancement of thin film photovoltaic paint. A mixture of quantum dot with perovskite also enhances the charge carrier extraction in harvesting layer of Quantum dot solar cell [28]. Perovskite solar cell also provide the flexibility of carrying high charge-carriers with the ability to allow electrons to travel more longer distance without much loss of energy [29]. A group of Organic solar cell also offers much cheaper and simpler photovoltaics with a compulsion of operation stability in high temperature environment. In addition, a material made up of Copper zinc tin sulfide (CZTS) also fulfills the material requirement for solution processable photovoltaic paints but it uses Selenium, being a relatively rare element, possibly could limit its versatility [30]. However, it has the potential to provide a new breakthrough in the efficiency of thin film paints by overcoming the limitation. The potential materials for photovoltaic paint could be QDSSC and perovskite, which offers unique properties in comparison with other materials, and are suitable to be investigated to increase the power conversion efficiency of photovoltaic paints.

Table 2: Material requirement for thin film photovoltaic paint

Material Requirement	Materials satisfying the requirement
Abundant material	CZTS, Perovskite.
Low-toxic material	CZTS, Quantum dot, Dye sensitized.
High temperature material	CIGS, CdTe, Quantum dots, Dye sensitized, Perovskite.
Solution processable	Organics, Perovskite, CIGS, CdTe, Quantum dots, Dye sensitized, CZTS
Suitable bandgap	CdTe,CIGS, CZTS, Dye sensitized, Perovskite.
Bulk heterojunction	Organics.
Low-cost synthesis	CdTe, CIGS, Pervoskite, CZTS, Quantum dot, Dye-sensitized.
Roll to roll	Organics, Perovskite, Dye sensitized, CIGS, CdTe, Quantum dot.
Mechanical Stability	Perovskite, Organic.

2.4. Integration of thin film technology

Thin film provides a way to synthesize solution based solar paints. This technology has been adopted due to its characteristics features i.e. use of minimum material with promising efficiency [31]. The aim of thin film integration in solar technology is to fulfill the requirement of light weight, low cost and bulk area processing [32].

The techniques employed for fabricating solution based solar cell are usually casting method such as doctor-blading, spin-coating, slot-die coating, screen printing, ink jet printing, spray coating [33-35]. The key requirements for the formation of layer by using any of the above-mentioned printing methods highly depend on the ink formulation. Inks having uniform quality, less density defects, sustainable shelf life, high concentration, uniform temperature gradient and high viscosity are reliable. Another important parameter is drying rate of ink (preferably having shorter drying steps). On the other hand, substrates of high uniformity and favorable surface properties are also required. Each solution processable method has its own attractive features. However, selection of each method depends on the product output. Some methods give high power conversion efficiencies but lacks large-scale manufacturability. Other provides bulk volume production but produces insufficient increase in power conversion efficiencies.

When the researcher compared the large area coating method (spray coating and slot-die coating) with that of small area (spin coating), the outcomes clearly shown the dependability of coating method on the film roughness, structure, morphology and density. Consequently, this affects the opto-electrical properties of the final product [35]. A comparative analysis of different power conversion efficiencies of the resulting products made from the solution processed methods is listed in Figure 3 [32].

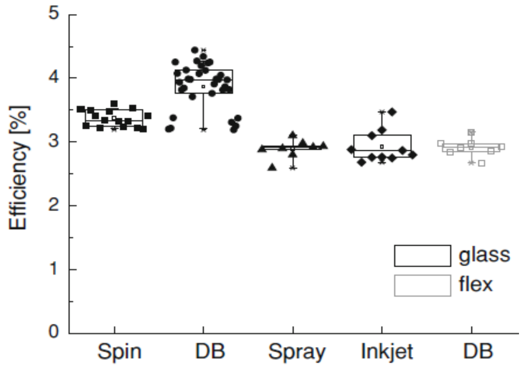

Fig. 3: Comparison of different power conversion efficiencies of solution processed methods. The black color shows the glass substrate and the gray box shows the flexible plastic substrate [32]

Depending on the process adopted, Power conversion efficiencies (PCE) of these methods ranges from 3% to 5%. Spin coating and doctor blade coating methods are among the top in efficiencies. In terms of controlling the thickness and uniformity of film, spin coating is suitable but causes problems in large-scale production and shows incompatibility to some extent with roll-to-roll production setup. Among others, Spray coating has the capacity to fabricate thin film in high output and roll-to-roll process due to its multiple step formation [42]. A brief benefits and disadvantages of different solution processed methods are mentioned in Table 3.

Table 3: List of solution processed methods with their pros and cons.

Solution Processed Method	Advantages	Disadvantages	Reference
Spin Coating Centrifugal acceleration causes solution to spread on high spinning substrate.	Homogeneity of film. Low defect density.	Adjustment problem with roll-to-roll setup. Small area processing.	[32]
Doctor blading Coating knife used to deposit solution onto the substrate.	Loss of deposit layer is reduced as compared to spin coating. Higher performance in comparison with spin coating.	Adjustment problem with roll-to-roll setup. Small area processing.	[36]
Screen Printing Image is patterned on the screen and selected area is exposed. Solution is spread on the screen and transfer on the substrate.	Compatible with roll-to-roll setup. Produces high resolution results	Highly viscous solution required. Requires stability of ink.	[37]
Spray Coating Droplets of solution are transferred onto substrate by high pressure gas with high velocity.	Highly compatible with roll-to-roll process. Multiple functional layers can be deposited	Ink must be compatible with airbrush system. Resulting Surface have some roughness.	[38]
Inkjet printing Ink is deposited on the substrate by writing head without being directly contacted with the surface.	Post-patterning of coated film is not required. Compatible with various substrates and roll to roll setup	Nozzle blockage by highly concentrated solution. Variation of droplets vary the thickness of film.	[39]
Slot die Coating Ink falls from a slot orifice by gravity onto the substrate.	Produces high quality films with much lesser defects. Wide range of ink viscosities can be used.	Incompatibility with patterning. Material loss increases at higher speed.	[40]
Successive Ionic Layer Deposition Adsorbed cations react with anions dispersed in precursor solutions to form a film.	Thickness and morphology of film can be controlled by varying the process parameters	Requires extensive time	[41]

The selection of a specific deposition technique requires various criteria and considerations such as application of thin film paint, characteristics of material and process technology. It also depends on the researcher to select more appropriate technique according to the area of application in which it can be utilized.

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2.5. *Reported efficiencies*

Transformation of solar energy in the form of paint has been very attractive. Due to different technological barriers, the progress in this area has been very limited [43]. Solar paint is a one-layer concept that can fulfil the demand of solar technology. It is one of the applications of nanoscale semiconductors. A researcher group has introduced an idea of generating solar energy from moisture by making a material using titanium oxide with molybdenum sulphide [44]. Other researchers used Nanocrystal based solar inks, QDSSC, DSSC, Perovskite, and Organics to make thin film photovoltaics paints. It can be seen from Table 4 that the most common deposition techniques are spin coating and spray coating for solar nano ink. Nanoparticulate organic photovoltaics (NPOPV) are also used to synthesize water based photovoltaic paints by conventional nanoparticle synthesis techniques. Some other deposition method such as SILAR, screen-printing and spin coating are used to deposit quantum dot based thin films. Few other methods are doctor blade for making dye-sensitized solar cells. The highest efficiency is achieved from spin coating method and the lowest from the NPOPV based organic photovoltaic paints. It can be found from the table that there is no general guideline available for choosing the best method to enhance the efficiency. However, type of material, substrate and utilization of final product allows the researcher to select more appropriate technique for making a highly efficient thin film photovoltaic paint. A summary of the effectiveness of solar paint based on different types of materials and techniques are listed in Table 4.

Table 4: Effectiveness of solar paint

Cell Configuration	Type	Deposition Method/ *Synthesis method	V_{oc} (mV)	J_{SC} (mA/cm^2)	FF	η (%)	Year	Reference
ZCISe	Quantum dot	Screen printing	590	11.11	0.63	4.13	2018	[43]
Pbs coated p-TiO_2	Quantum dot	p-SILAR	494	5.23	0.52	1.35	2017	[45]
$CsPbBr_3$	Perovskite	Spin coating	1500	5.6	0.62	5.4	2016	[46]
CdS-CdSe/ZnO	Quantum dot	Mix	320	10`	0.36	1.36	2016	[47]
TiO_2/tBA	Dye Sensitized	Doctor blading	750	10.3	0.63	5.0	2015	[48]
$Cu_2ZnSnS_{4x}Se_{4(1-x)}$	Nano ink	Spin coating	410	32.9	0.57	7.68	2014	[49]
P3HT:ICBA	Organic	*Precipitation	781	9.00	0.58	4.10	2014	[50]
P3HT:PCBM	Organic	*Precipitation	634	4.84	0.36	1.09	2014	[51]
P3HT:ICBA	Organic	*Miniemulsion	791	5.57	0.57	2.50	2013	[52]
PFB:F8BT	Organic	*Miniemulsion	1500	1.81	0.30	0.82	2012	[53]
CdS-CdSe/TiO_2	Quantum dot	p-SILAR, Mix	585	3.1	0.59	1.08	2012	[54]
Cu(InGa)Se_2	Nano ink	Spin coating	305	17.3	0.50	2.6	2011	[55]
CdTe	Nano ink	Spin coating	590	20.7	0.56	6.9	2011	[56]
PbS/ PEDOT:PSS	Quantum dot	Spin coating	910	3.7	0.37	1.27	2011	[57]
$CuInSe_2$	Nano ink	Spray coating	410	16.3	0.46	3.1	2010	[58]
PbS	Nano ink	Spin coating	460	14.45	0.60	3.93	2010	[59]
PbS/TiO_2	Quantum dot	Spin coating	510	16.2	0.58	5.1	2010	[60]
CZTS	Nano ink	Chemical bath	430	31.2	0.53	7.23	2010	[61]

IV. CONCLUSION

Thin film has provided a way to convert the concept of solar paint into reality. In this paper, a brief study of the previous literature is discussed with the aim of highlighting the problems related to efficiency. The selection of material and deposition technique plays a vital role in the development of efficient photovoltaic paint. Quantum dots and Pervoskite based thin film photovoltaic paints can provide a way to enhance the efficiency. Similarly, spin coating deposition technique seems to be more suitable for future studies.

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