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Citation: Zhang, T., Iqbal, S., Zhang, X-Y., Wu, W., Su, D. & Zhou, H-L. (2020). Recent advances in highly efficient organic-silicon hybrid solar cells. *Solar Energy Materials and Solar Cells*, 204, 110245. doi: 10.1016/j.solmat.2019.110245

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Link to published version: <https://doi.org/10.1016/j.solmat.2019.110245>

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Recent advances in highly efficient organic-silicon hybrid solar cells

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ARTICLE INFO	ABSTRACT
<i>Keywords:</i> Organic-silicon hybrid solar cells Efficiency enhancement Light trapping Surface texturing Metallic nanostructures	Organic-silicon hybrid solar cells (organic/Si HSCs) have drawn much attention in the development of modern low-cost photovoltaic solar cells. Due to simpler and less expensive fabrication processes at room temperature, the HSCs have many superiorities over conventional silicon solar cells, positioning the HSCs be a striking research topic. Recently, a significant amount of research has been done to improve the yield and efficiency of hybrid solar cells. The performance enhancement of hybrid solar cells highly depends on a combination of the electrical, optical, materials and structural aspects. This review is dedicated to the recent advances in the mechanism, fabrication processes and light management in organic/Si HSCs, highlighting the important device structures, the surface texturing, the transparent electrodes as well as the integration of metallic nanostructures to improve the performances of hybrid solar cells.

1. Introduction

Growing energy demands and global environmental changes are the two critical factors for the survival and sustainability of the human race. As the production of energy from fossil fuel (coal and oil) generates harmful emissions to the environment, has a harmful impact to mankind directly and indirectly [1,2]. Photovoltaics (PVs) is considered to be one of the most promising clean technologies that can overcome both concerns [3,4]. Though solar is a clean and environment friendly energy resource, it is very challenging to achieve high performance and low cost [1,5]. Many researchers are working to develop new technologies that may become worldwide renewable energy solutions in the future [6]. Photovoltaics have high potential output ratio, compare to other energy conversion methods [3,7] such as fuel energy by photosynthesis, or solar thermal energy harvest [8]. However, the output ratio is still quite low, the stability is also a matter of concern such as photothermal stability and stability of PEDOT:PSS for a long time leaving plenty of room for the improvement [9]. Because the stability of the polymer-based photovoltaic device in air ambient environment is an important issue to [10]. So, the organic/Si PV is an attractive topic for researchers.

Currently, the commercial PV market is restraint to the crystalline silicon solar cells a considerable market shares up to 90% [11]. There is no doubt they exhibit high efficiencies in the commercial industry, but the expensive materials cost, complicated fabrication, and energy consuming process are few limitations which make an Organic/Si HSCs a competitive research direction to the conventional silicon solar cells [12–14]. Therefore, many researchers show more interests in organic solar cells, organic-silicon hybrid solar cells (organic/Si HSCs) which may reduce the time and cost required to fabricate photovoltaic cells [9,15]. The hybrid SCs are fabricated by using crystalline silicon with conjugated polymers (such as poly(3,4 ethylene dioxythiophene styrene sulfonate PEDOT:PSS) [16–18] making it be

simpler and easier to produce solar cells utilizing nontoxic, low cost materials at room temperature. It is also possible to prepare flexible solar cells with large area low cost technologies such as printing and roll to roll processes [19–22]. Conjugated materials i.e. PEDOT:PSS, poly(3-hexylthiophene) (P3HT) [23–25], phenyl-C61-butyric acid methyl ester (PCBM) [26,27], as well as many others materials, have been studied extensively due to their ability to generate inexpensive power at higher efficiencies [16,28–33]. Advances in the synthesis of organic materials and the development of new device structures for HSCs enable to achieve the efficiencies of 17.4% (with *n*-type Si substrate) [34]. Nevertheless, to compete with conventional silicon solar cells, furthermore, studies are required to increase the output efficiencies, to enhance the stability and reduce the cost of organic/Si HSCs. Because stability is another major concern that limits the suitability of hybrid solar cell device for commercial applications [35]. To this point, the issue of stability for PEDOT:PSS/*n*-Si hybrid solar cells in an operational environment still remains a challenge [36][10][9]. Many researchers are studying new materials and effective methods to improve the stability of the HSCs [37]. For example, Schmidt practice capping to the entire solar cell device by atomic layer deposition of an aluminium oxide film with which they have reported high Voc of 690mV and PCE of 12.3% [38]. While Jian He studied the formation of conformal heterojunction coating and moisture-resistant capping layer by employing diethyl phthalate (DEP) as a conformal contact between PEDOT:PSS film and textured Si with pyramids. They claim to achieve high Voc 634mV and PCE of 16.2% with improved stability of the fabricated device [37]. In this paper, we summarize the basic knowledge, the structures, the different fabrication processes, the incorporation of metallic nanoparticles and mechanisms of the organic/Si HSCs.

2. Organic/Si hybrid solar cells

The maximum reported efficiency of the silicon solar cell is 29.43% [39]. However, hybrid SCs have lower reported efficiency as compared to Si SCs. The highest laboratory efficiencies for single crystalline silicon solar cells have been in the range of 26.7% [28,40,41], while that of hybrid organic/Si SCs have demonstrated up to 17.4% (with *n*-type Si substrate) [34] and 20.6% (with *p*-type Si substrate) [42]. The average stabilized efficiency of commercial c-Si solar cells produced at large scale have an efficiency of 22.8% according to ITRPV data published in March 2018 [43].

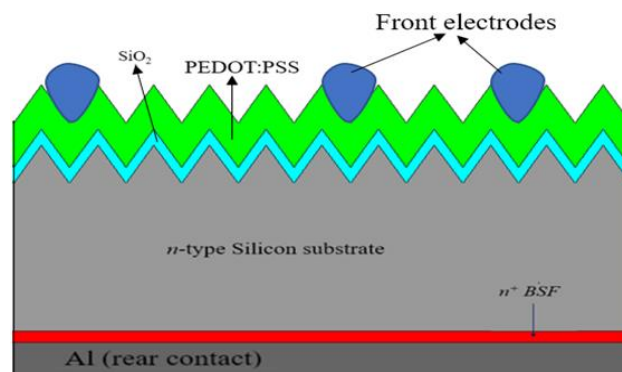


Fig. 1. Schematic of an organic-silicon hybrid solar cell on *n*-type silicon featuring a random-pyramid-textured front surface with a SiO_x tunnelling layer and n⁺ BSF [38].

A typical hybrid HSC device is made of crystalline-Si with a pyramidal surface, coated with PEDOT:PSS as hole conducting layer. This configuration can provide an energy efficient transformation with significantly reduced cost and enhanced power conversion

efficiency from 8% to 12% [32,33,38,44–47]. Fig. 1 illustrates the schematic of pyramidal front surface organic/Si solar cell, containing a top layer of PEDOT:PSS and thin layer of native oxide (SiO_x) acting as tunnelling layer, n -type silicon substrate, n^+ BSF (back surface field) to improve the carrier collection and aluminium as rear electrode for the electrical connecting to the load [48].

2.1 Performance enhancement of organic-silicon heterojunction solar cells by front surface treatment and different texturization techniques.

Recently, many efforts have been made to explore the favorable characteristics of both organic-silicon in the fabrication of hybrid solar cells [49–54]. Surface texturing of silicon wafers has been always a winning technique to improve light management and enhance the performance of the photovoltaic device [46,55]. In addition, refining the adhesion of PEDOT:PSS and silicon at the interface for charge separation as well as carrier transportation to improve PCE [56–58]. Many efforts have been made to harvest solar energy by exploiting the combination of surface texturing of silicon which can perform a principal role in improving the efficiency of the solar cell device [59–62]. Recently, extensive studies and analysis have been carried out specifically using silicon surface texturing to improve light trapping and absorption properties of organic/Si HSCs [56,63–66]. Surface treatment and texturization has been widely adopted with a purpose to ensure the enhanced HSC device (amorphous/crystalline) fabrication with improved conversion efficiency. Surface treatment/texturization of silicon substrate is used to reduce the front surface reflection and enhance the absorption by light trapping due to micro and nanostructured silicon surface in HSCs [46,67,68]. Texturization of silicon has shown much better results as compared to conventional planar surface hybrid solar cells. Many researchers have studied surface treatment and different texturing techniques which includes front surface etching, micro/nanotexturing and antireflection coating, silicon nanoholes, SiNWs, micro pyramids to enhance the overall performance of solar cell device by reducing the front surface reflection, enhancing absorption, light trapping and management of the solar cell in which few of them will be discussed in this section.

S. Kim et. al [69] studied the integration of silicon nanoparticles (Si-NPs) in the organic/Si photovoltaics as a replacement of chalcogenide nanocrystals, which have been widely used in this type of solar cells. PEDOT:PSS and PCBM were employed as hole and electron transport layers, respectively. Testing results indicate that open circuit voltage (V_{oc}) fundamentally relies on the size and volume fraction of Si-NPs. These results imply that the small size of Si-NPs and amorphous phase structures led to bandgap widening and ultimately resulted in increased V_{oc} while coupled with PCBM acceptor. The device achieved the highest V_{oc} of 0.634 V when the Si-NPs of 5.7 nm were used, with a power conversion efficiency (PCE) of 0.05%. Silicon nanowires (SiNWs) have also been studied extensively due to its light trapping property [44,70]. H. J. Syu et. al [71] studied the properties and solar cell applications of SiNWs and PEDOT:PSS. Light trapping and absorption can be enhanced by altering the length of the SiNWs, which can also increase the junction area. Conversely, the length of SiNWs is not the only factor that affects the performance of the SC device. In fact, long SiNWs tends to combine at the top position making the penetration be difficult for PEDOT:PSS, leading to weak adhesion at the junction while the increased number of SiNWs decreased the lifetime of minority carriers. SiNWs with the length of 370 nm provided largest short circuit current density of 24.24 mA cm^{-2} , a high open circuit voltage of 0.532V and the highest PCE of 8.40% in comparison with devices using SiNWs of other lengths. While Z. Ge et. al [72] fabricated silicon nanowires/cadmium telluride quantum dots (CdTe QDs)/PEDOT:PSS heterojunction solar cells. Uniformly distribution of CdTe QDs on SiNWs made an easy filling of PEDOT:PSS in the spaces between SiNWs. Figure 2 shows the

schematic of a solar cell with incorporated CdTe QDs between the SiNWs. Experimental results demonstrate that the performance of the device with CdTe QDs layer had a noticeable enhancement. The short circuit current (J_{sc}) achieved is 33.5 mA/cm^2 , which is 15.1% enhanced than that of an SC without CdTe QDs. Power Conversion Efficiency (PCE) also increased by 28.8%, which is 7.6%. The enhancement in the performances are attribute to the down-shifting effect of CdTe QDs and alteration of SiNWs with CdTe QDs. These results suggest that the incorporation of CdTe QDs in SiNWs is a favourable contender for organic/Si HSCs.

Q. Liu et. al investigated PEDOT:PSS/poly-Si (*n*-type) HSCs, fabricated by the Chemical Mist Deposition (CMD), high-pressure H_2O vapor was used to treat *p*-Si before the deposition of the organic thin film [73]. Treating *p*-Si with high pressure H_2O effectually trim down the dangling bonds, enhancing the charge carrier collection, transportation and reducing recombination at the PEDOT:PSS/*p*-Si junction. The silicon substrate was enclosed to the direct flow of pressurized H_2O to achieve more enhanced and smoother surface [74]. Compare to spin coated devices, the ones fabricated by the CMD proved to have steadier photovoltaic performance achieving a power conversion efficiency (PCE) of 9.7%, with a short circuit density of 33.5 mA/cm^2 , an open circuit voltage V_{oc} of 540 mV and fill factor of FF 0.53. These results indicate that the use of negatively charged mist precursor significantly enhanced the junction bonding between PEDOT:PSS and *p*-Si, which improves the carrier collection efficiency in the devices.

Schmidt [48] investigated the electronic properties of *c*-Si/PEDOT:PSS by contactless lifetime carrier measurements. They deposited back surface field (BSF) by phosphorus diffusion from POCl_3 source using the quartz-tube furnace at $850 \text{ }^\circ\text{C}$. Wet etching done by using a KOH aqueous solution to form the random pyramid (RP) structures, the native oxide was grown as a passivation layer. Their results demonstrate high open circuit voltage V_{oc} 603 mV. While RP surface benefits in reducing solar cell surface reflectance and improve light trapping, resulting in $J_{sc} = 29.0 \text{ mA/cm}^2$, fill factor (FF) of 70.6 and power conversion efficiency of 12.3% [38].

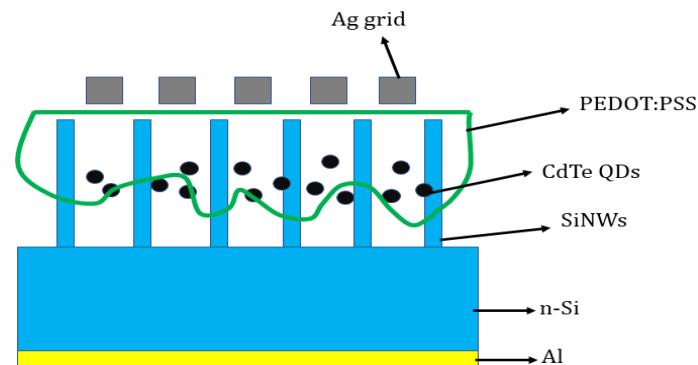


Fig. 2. Depicts schematic of hybrid SC silicon/PEDOT:PSS with intermediate CdTe QDs layer [72].

Hong et. al [75] fabricated a new structure based on silicon nanoholes (SiNH) filled by the PEDOT:PSS. This structure was fabricated by electroless chemical etching using silver nanoparticles as a catalyst, while *p-n* junction is formed by spin coating of PEDOT:PSS on the SiNHs. Solar cell performance was optimized by changing the depth of SiNH, different depths of SiNHs were obtained by varying chemical reaction time. The highest power conversion efficiency of 8.3% was attained with the hole depth of $1 \text{ }\mu\text{m}$. Moreover, in comparison with SiNWs and polymers, they have lower material cost and easier fabrication advantages [75–77]. As single standing SiNW tend to break and also aggregation occur when

the length is increased. These results demonstrate that SiNH structure has robust antireflection and light trapping properties that can conquer the shortcoming of SiNWs.

Jian He et. al [77] investigated the treatment of *n*-Si wafer using tetramethylammonium hydroxide (TMAH) solution and also applying a copper iodide (CuI) capping layer on the PEDOT:PSS to get the Schottky junction with lowest energy barrier height. Analysis of photoelectric characteristics demonstrated that surface recombination and defects were significantly suppressed due to the TMAH treatment, resulting in an increased thickness of the interfacial oxide layer. While the CuI capping layer caused a strong reversal layer closer to the *n*-Si surface, resulting in excellent passivation. With improvements in the interfacial layer and passivation, an open circuit voltage of 0.656 V_{oc} , fill factor of 78.1% and a stable power conversion efficiency of 14.3% was achieved for a planar *n*-Si/PEDOT:PSS HSCs.

Thiyagu and Hsueh et. al [78] studied hierarchical surface silicon nanoholes in the form of micro desert textures. Si/PEDOT:PSS with hierarchical surface offer brilliant light absorption of 97% from 300 nm to 1100 nm for the spectral range at a thickness of 60 nm internal reflection caused by subwavelength of Si nanoholes and micro-deserts textures. According to the angle of incident (AOI) the reflectance is less than 1% although the angle is 75°. Their solar cells demonstrated an amazing power conversion efficiency of 12%.

Table 1. Efficiency comparison of solar cells measured at one sun(100mW/cm²). Planar SC [32], Random Pyramid (RP) [53], SiNWs [70], SiNHs [75], Chemical Mist Deposition [73] and Si-NPs [69] fabricated by different Processes and methods.

Device Structure	J_{sc} (mA/cm ²)	V_{oc} (mV)	FF [%]	η [%]	Ref	Year
Si-NWs (In:Ga/SiNWs/spiro-OMeTAD/PEDOT:PSS/Cu (core shell))	31.3	527	58.8	9.70	[70]	2011
Planar SC (Al/PEDOT:PSS/Si)	24.53	470	55.0	6.40	[32]	2013
Si-NPs (Al/PCBM/SiNP/PEDOT:PSS/ITO/Substrate)	30.8	634	26.0	0.05	[69]	2013
Random Pyramid (Al/PEDOT:PSS/SiO ₂ /Si)	29.0	603	70.6	12.3	[53]	2014
Si-NH (Ag/PEDOT:PSS/SiNH/Si/Al)	25.0	550	60.4	8.3	[75]	2014
CMD (Ag/PEDOT:PSS/Si/InGa)	33.5	540	53	9.7	[73]	2014
Nanostructured Si Schottky junction (Ag/PEDOT:PSS/Si/Cs ₂ CO ₃ /Al)	32.2	621	68.8	13.7	[56]	2015
SiNH Interfacial Conformal layer (ITO/PEDOT:PSS/LPD-TiO ₂ /Si/Al)	35.91	630	65	14.7	[80]	2016
SiNT Array (Ag/PEDOT:PSS/SiNT/Al)	29.9	510	65.7	10	[65]	2014
Transport mechanism (N_D [cm ⁻³] 1.6×10^{17})	29.1	634	75	13.9	[81]	2015
Pyramid with DEP coating (DEP/PEDOT:PSS/ <i>n</i> -Si/ <i>a</i> -Si(H) <i>i</i> / <i>a</i> -Si(H) <i>n</i> /Al)	36.5	634	70	16.2	[37]	2017
Polymer Nanocomposite Top Electrode (M-MPNTE/Ag/Au+MoO _x /Al4083/E-inversion layer/ <i>n</i> -Si/Al)	17.91	605	80.2	8.70	[58]	2018
BackPEDOT concept (SiN _x /Al/Al ₂ O ₃ / <i>n</i> ⁺ FSF/Si/SiO _x /Ag)	38.9	657	80.6	20.6	[42]	2015

J. Zhu et. al studied novel double layer (DL-PEDOT:PSS) structure employing high work function (HW) PEDOT:PSS (AI 4083) as the middle layer and highly conductive (HC) PEDOT:PSS as the top layer on the *n*-type Si substrate [79]. The DL-PEDOT:PSS structure

suppressed the Si surface recombination, due to strong inversion layer formed. A device with DL-PEDOT:PSS mixed with 7% wt Ethylene glycol (EG) demonstrates improved V_{oc} of 640 mV, FF of 0.755, J_{sc} of 26.27 mA cm⁻² with remarkable enhancement in the efficiency of 12.69%. This method proves the potential of DL-PEDOT:PSS for the strengthening of the inversion layer at the silicon surface and for the passivation of p -type contact in the next-generation hybrid photovoltaic devices.

Cosme et. al [82] fabricated thin film solar cells from hydrogenated silicon (Si:H) with organic P3HT:PCBM and PEDOT:PSS films. The organic thin film was deposited with spin-coating, after that, it was exposed to precursors to coat Si:H films using RF-PECVD with low deposition temperature $T_d = 160$ °C. Various combinations of materials in different layers were studied, (a) ITO/(p)SiC:H /P3HT:PCBM/(n) Si:H, (b) ITO/PEDOT:PSS/(i)Si:H/(n) Si:H and (c) ITO/PEDOT:PSS/P3HT:PCBM/(i)Si:H/(n) Si:H. The hybrid device shows enhanced optical responses of 50%-80% absorption in the photon energy range of ~ 3.1 -3.5 eV in comparison with the reference device. The hybrid device of ITO/PEDOT:PSS/(i) Si:H/(n)Si:H demonstrates amazingly high J_{sc} of 17.74 mA/cm² a V_{oc} of 640 mV, FF of 0.67 and PCE of 3.75%. Table 1. summarizes the comparisons of different organic/Si hybrid solar cells with their respective V_{oc} , J_{sc} , FF, and PCE.

2.2 The Back-junction organic/Si hybrid solar cell for lower parasitic absorption.

D. Zielke et. al [31,42] proposed the back-PEDOT concept by employing PEDOT:PSS on the rear side instead of the front side of a silicon substrate. They managed to significantly reduce the parasitic light absorption in the PEDOT:PSS, resulting into the improvement of short circuit current (J_{sc}) of 39.7 mA/cm² and open circuit voltage (V_{oc}) of 663 mV, respectively. Although the series resistance was comparatively high (2.88~3.35 Ω cm²), impressive power conversion efficiency of 17.4% was still achieved. The measured quasi efficiency of this device is 21.2%, implying that the back-PEDOT concept certainly works for high efficiency, easy and low-cost fabrications of solar cells. Figure 3 illustrates the schematic of back-PEDOT solar cell device with PEDOT:PSS spin coated on the rear side of the device. Table 2 illustrates the improvements and evolving work done on organic/Si hybrid solar cells over time. It also summarizes the fabrication process and achieved an enhancement in V_{oc} , J_{sc} , FF, and PCE.

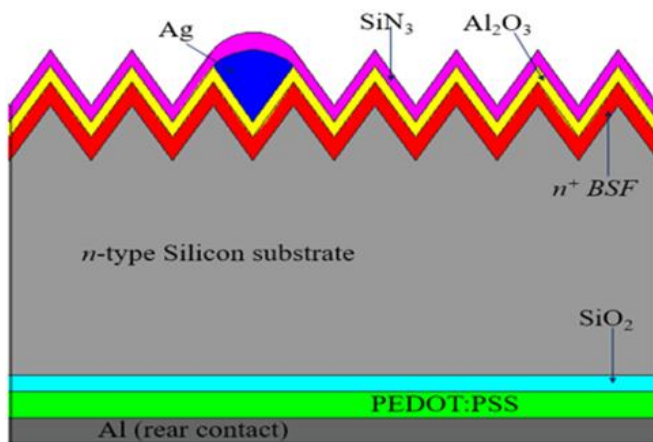


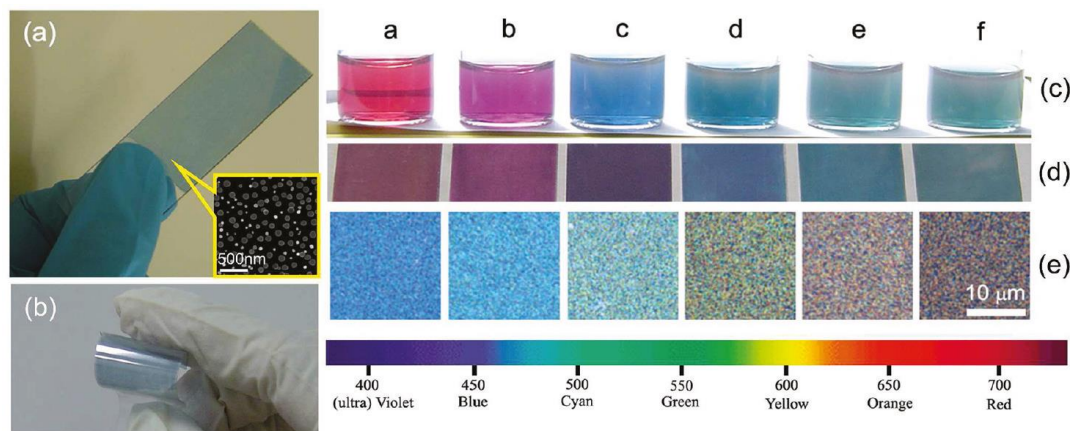
Fig. 3. Illustration of back-junction (“BackPEDOT”) solar cell on n-type silicon. [42]

Y. Liu et al. fabricated HSC devices with integrated triboelectric nanogenerator (TEG) to harvest energy from both sunlight and raindrops [83]. HSC was fabricated with TENG by the

mutual electrode of PEDOT:PSS film. They develop a single electrode mode waterdrop TENG on SC by combining imprinted polydimethylsiloxane (PDMS) as triboelectric material with PEDOT:PSS layer as an electrode. Due to increased contact area between PDMS and waterdrops significantly improve output TENG and overall efficiency of SC device up to 13.6%, with V_{oc} of 0.628, J_{sc} of 29.1 mA/cm².

3.0 Highly-efficient hybrid solar cells with integrated metallic nanoparticles

From the last 10 years, the potential of plasmonic (metallic) nanoparticles have been widely studied by researchers for solar energy to electrical power harvest, and solar to chemical fuel conversions [84]. Plasmonic HSCs are devices with incorporated metallic nanoparticles in the PEDOT:PSS layer which can enhance the photoelectric conversion with the help of plasmonics effect [85,86]. Characteristically they are up to $< 1\sim 2 \mu\text{m}$, while theoretically, they could be as small as 100 nm [87,88]. As complete absorption is a challenge



in organic/Si HSCs, so techniques of light trapping and Near InfraRed (NIR) harvesting are essential for efficiency enhancement [89,90].

Fig. 4. (a) silver (film) nanostructure film on a glass substrate and its SEM image (b) Silver nanostructures on a flexible polymer substrate (c, d) diluted silver colloids and silver film containing SNPs of different sizes (e) Optical microscopic images of the SNP films under white light illumination [91]

3.1 Metallic nanostructures for highly efficient plasmonic organic/Si HSCs.

Localized surface plasmon resonance (LSPR) is achieved in organic/Si SCs by incorporating metallic nanostructures in the organic solution layer (PEDOT:PSS). It is an interesting approach towards the solution processed hybrid organic/Si solar cells to enhance the output efficiency [89]. Several types of synthesized metallic nanostructures, i.e. spherical, pyramids, thin plates with a triangular, and other shapes of various sizes, with tunable resonance wavelengths have recently been studied [92–96]. Effortless solution processed fabrication makes them considerably more adoptive to be employed in organic/Si HSCs [97,98]. Wet chemical synthesis process makes possible the huge manufacturing of pure metallic nanocrystals with various types, sizes, shapes and dispersal [99–101] which can be easily incorporated in organic/Si HSCs to benefit from its plasmonic effect [102–106].

Z. Tang studied PEDOT:PSS/c-Si solar cell with and without gold nanoparticles (AuNPs) incorporation into PEDOT:PSS layer of the fabricated devices with 10–15% AuNPs incorporation achieve an efficiency of 10.28% [107]. Which is about 10% enhancement as compared with the reference cell without AuNPs, which is 9.29%. Efficiency enhancement is due to the local surface plasmon resonance (LSPR) generated by incorporation of AuNPs is

thought to be the reasons for the improvement in short-circuit current density. AuNPs also enhance the carrier collection efficiency which leads to the improvement of the whole PCE of the solar cell device of 10.30%, FF of 71%, V_{oc} of 534 mV and J_{sc} 27.15 mA cm⁻². However Z. Xia studied the incorporation of gold nanoparticles (AuNPs) into PEDOT:PSS/Si HSCs [1]. Their device with optimized size of AuNPs achieved a PCE of 12.9%. They incorporated different sizes of AgNPs to study device performance improvement. From experimental numerical simulation results the improvement in efficiency is accredited to the light scattering and local electromagnetic field enhancement generated due to AgNPs excitation of localized surface plasmon resonance. With 40nm of AgNPs they achieved FF of 75%, V_{oc} of 619 mV and J_{sc} 27.79 mA cm⁻². While Lee et. al studied the scattering and absorption by modeling different sizes of isolated Ag nanostructures in the PEDOT:PSS and studied the ratio of scattering to absorption for the solar spectrum of 300 nm to 800 nm using NPs of various sizes [110]. Small AgNPs (~ 40 nm) transcend the scattering power while increasing the size of NPs induced scattering enhancement. This proved that comparatively larger AgNPs are more suitable. Scattering direction is also an important parameter that must be considered since the active layer will not absorb the backward scattering [111–114]. Moreover, the fraction also increases with the increasing size of AgNPs, it was stabilized with the diameter of ~75nm for AgNPs. The ratio of scattering to absorption is given by the equation $S = \delta_{scat}/\delta_{abs}$, where δ_{scat} for both near-field and far field scatterings from nanostructures, which must satisfy the condition of $S \gg 1$ [115].

Many researchers also reported good results from the incorporation of AgNPs with a decreased sheet resistance of PEDOT:PSS. I. Khatri reported enhancement of PEDOT:PSS/*n*-Si solar cell by integrating silver nanoparticles (AgNPs) in PEDOT:PSS [108]. The device with AgNPs show PCE of 10.21% which is higher as compared to the original SC device without AgNPs. They also reported a decrease in sheet resistance with enlarging surface roughness of PEDOT:PSS thin layer for efficient charge collection with V_{oc} of 510 mV and J_{sc} 27.27 mA cm⁻² and FF of 72%. While looking at the FF and J_{sc} there is not much difference with the work done by Z. Tang [107] though both the NPs are made up of different materials. While some researcher reported the absorption effect of AgNS on a planar SC device such as L. Hong investigated insertion of periodic silver nanospheres on planar PEDOT:PSS/Si HSC device to study the absorption enhancement due to the plasmonic effect [109]. Periodicity and diameter of AgNS on light absorption was studied thoroughly with finite element method. Improvements in light absorption was found at periodicity of 600 nm with maximum efficiency of 22.6% which is 23.8% higher than that of planar HSC without AgNS.

H. S. Noh et. al [125] examine the plasmonic effect in bulk organic/Si HSCs using poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) by embodying silver nanoprisms (Ag NPSs) in a poly(3,4-ethylenedioxy thiophene) (PEDOT) buffer layer. Geometrical characteristics and absorption of NPSs were studied for tuneable in-plane dipole local surface plasmon resonance (LSPR). Results demonstrated that the PCE of solar cell device was improved due to an upsurge of short-circuit current (J_{sc}) in comparison with a reference device almost without any deviation in electrical properties. It was noted that the efficiency of the solar cell decreases by increasing the periodicity of Ag NPSs and the P3HT:PCBM active layer, implying that the enhanced photocurrent and optical absorption due to near field enhancement of the Ag NPSs. LSPR strongly relies on the size, shape, allocation, area coverage and density of metallic nanostructures, as well as the refractive index of the medium [126,127]. By the alterations of these parameters, we can achieve LSPR

at our desired wavelengths [128]. Besides, other nanostructures such as nanorods, nanospheres, nanoprisms and nanostars have also been employed for the plasmonic enhancement in hybrid solar cells. [129–134]

Table 2. describes the development of hybrid heterojunction organic/Si solar cell over time.

Improvement and novelty work	Device structure	J_{sc} A/cm ²	V_{oc} mV	η %	FF %	year	Ref.
Silicon wafer as base material	(Ag/PEDOT:PSS/P3HT/Si/Al)	29.0	590	10.1	59.0	2011	[116]
Native SiO _x as passivating interface between silicon and PEDOT:PSS	(Ag/PEODT:PSS/n-Si/Ti/Pd/Al)	26.3	600	11.3	70.9	2012	[33]
Random-pyramid-textured front surface and back-surface-field	(Ti/Pd/Ag/PEDOT:PSS/SiO _x /Si/n ⁺ /Al)	29.0	603	12.3	70.6	2013	[48]
Nanowire Hybrid Solar Cells: Significance of Strong Inversion Layer	(Ag/PEDOT:PSS/SiNWs/Si/Al)	30.42	614	13.1	70	2015	[117]
High-Efficiency Silicon/Organic Heterojunction Solar Cells with Improved Junction Quality and Interface Passivation	Cu/Ag/PEDOT:PSS/SiO _x /Si/InGa	28.0	656	14.3	78.1	2016	[77]
Improved PEDOT:PSS/c-Si hybrid solar cell using inverted structure and effective passivation	(Ti/Ag/PEDOT/c-Si/i,a-Si(H)/ n,a-Si(H)/Al)	36	630	15.8	70.3	2016	[118]
16.2% Efficiency and Improved Stability by Formation of Conformal Heterojunction Coating and Moisture-Resistant Capping	(DEP/PEDOT:PSS/n-Si/a-Si(H)i/a-Si(H)n/Al)	36.5	634	16.2	70	2017	[37]
High Performance of PEDOT:PSS/n-Si Solar Cells Based on Textured Surface with AgNWs Electrodes	(AgNW/Ag/PEDOT:PSS/Si/Al)	26.55	510	8.54	62.13	2018	[13]
MoO ₃ Film as Antireflection and Inversion Induced Layer	(Ag/MoO ₃ /PEDOT:PSS/Si/Liq/Al)	29.2	630	13.8	74.9	2014	[119]
PEDOT:PSS/nanostructured by doping-free rear contact	(Ag/PEDOT:PSS/Si/Cs ₂ CO ₃ /Al)	32.2	621	13.7	68.4	2015	[120]
High Open-Circuit Voltage via Improving Junction Quality	(Ag/PEDOT:PSS+GOPS/nanostructured Si/Al hybrid)	30.2	640	14.1	72.8	2016	[121]
Perovskite Nanoparticle Coating Introduces Polarization Enhancing Silicon Cell Efficiency	(Perovskite NPs/PEDOT:PSS/Ag/MoO _x /Si/Al)	30.84	635	14.3	73	2017	[122]
Buried MoO _x /Ag Electrode with a High Fill Factor	(PEDOT:PSS+TEOS/MoO _x /Ag/Si/Al)	28.3	635	14.2	80	2018	[123]
Vanadium Oxide as Transparent Carrier-Selective Layer in Silicon Hybrid Solar Cells	(Glass/ITO/Vox/PEDOT:PSS/SiNWs/Si/Al)	45.4	541	14.4	58.3	2019	[124]

3.2 Solution processed highly conductive transparent electrodes.

Recently, organic-silicon HSCs with a transparent conductive electrode and crystalline silicon have drawn interests of many researchers [33,44,135]. *N. Venugopal et. al* [136] fabricated a plasmonic heterostructure of Ag nanoislands/*n*-Al:ZnO/*p*-Si, processed by pulsed laser deposition (PLD) and thermal evaporation method. Al:ZnO (AZO) is used as a transparent conductive oxide (space layer) and as rectifying junction with silicon. Light absorption was noticed with the incorporation of Ag nanoislands on Al:ZnO. Electrical and optical parameters were examined and significant enhancement was observed in both visible and UV spectrum. The responses were also compared with a solar cell based on bare *n*-Al:ZnO/*p*-Si heterostructure. Deposition of Ag nanoislands enhanced the near band edge

emission, while the dark and illumination current density have also been improved. Fig. 5 illustrates a schematic representation of Ag nanoislands on top of *n*-Al:ZnO/*p*-Si heterostructure.

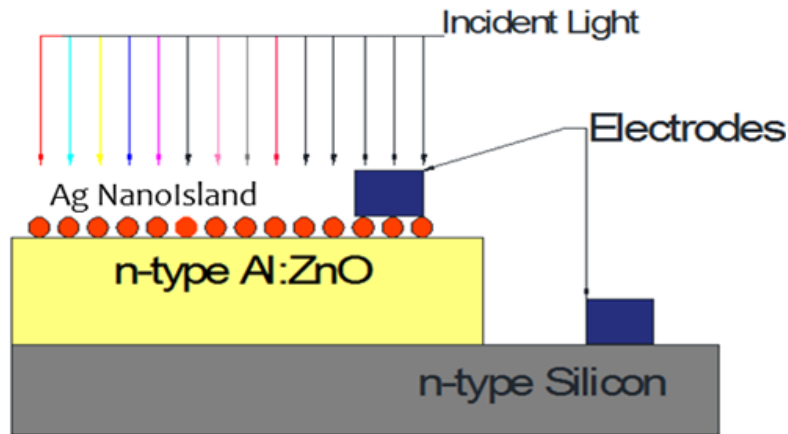


Fig. 5. Schematic diagram of Ag nanoisland/*n*-Al:ZnO/*p*-Si heterostructure. [136]

Xu et. al [11] fabricated solution processed silver nanowires (AgNWs) for the transparent conductive electrodes (TCEs) bonded with graphene oxide (GO), as a replacement of vacuum deposited metal grid. They developed a unique “sandwich” structure incorporating AgNWs network between PEDOT:PSS and GO with a figure of merit of $8.6 \times 10^{-3} \Omega^{-1}$ which was even higher than sputtered indium tin oxide (ITO) electrode ($6.6 \times 10^{-3} \Omega^{-1}$). High power conversion efficiency of 13.3% was achieved due to significant improvement of built-in voltage (V_{bi}) and low series resistance of TCEs. As the TCEs were prepared by a simple low-temperature solution process, it is a cost-effective process for mass production as well. The key benefits of these TCEs are their high transmission in the visible spectrum, low sheet resistance and higher work function [137]. On the other hand, Jiang et al investigated the silver nanowires as electrodes for the PEDOT:PSS/*c*-Si SC [13]. They studied AgNWs as an electrode because of its enhanced optical transmittance and better electrical conductivity. Highest PCE of 11.07% was achieved which show 29.6% enhancement in comparison with traditional Ag electrodes as they already fabricated with PCE of 8.54%. They claim that with PEDOT:PSS film and AgNWs transparent electrodes could be a capable contender towards highly efficient and low cost hybrid solar cells.

M. Chalh et. al [138] fabricated transparent electrodes from AgNWs and zinc oxide (ZnO) nanoparticles. By embedding AgNWs into ZnO they fabricated transparent multilayer electrode ZnONPs/AgNWs/ZnONPs (ZAZ) with a low sheet resistance of $13 \Omega/\text{sq}$ and an optical transparency of 88%. The optical parameters of ZAZ were simulated by FDTD. ZAZ multilayer electrodes were optimized and successfully integrated into organic/Si hybrid solar cells. PCE of 3.53% was achieved from the ITO-free solar cell and was compared with traditional ITO-based solar cells with an efficiency of 3.16%. These results suggested that ZAZ is a better substitute to ITO films for high performance inverted organic/Si HSCs, as it has enhanced transmission and favorable plasmonic effect. Researchers also reported Ag nanofilms with improved light absorption comparing with AgNPs. Such as Wang et. al [139] studied two-dimensional ultrathin gold nanofilms. Their results demonstrated that one and two-layer nano gold films have obvious enhancement of light absorption in the P3HT:PCMB and PEDOT:PSS based devices, showing high SPR compared to gold nanoparticles [51]. Due to the superior properties of SNPs and GNPs, they can be employed in organic/Si HSCs for

the absorption enhancement without altering the physical dimensions of the absorber layer, enabling new possibilities for the fabrications of highly efficient organic/Si hybrid solar cells.

4. Conclusion and outlook

Increasing power demands by consumers will always open opportunities for researchers to look for renewable energy resources and materials. Organic-Silicon HSC is a game changer in the photovoltaic industry as recent studies and analysis demonstrate advanced experimental results with improved light trapping, absorption, and performance enhancement. A collection of techniques and methods i.e. silicon surface texturing random pyramids, silicon nanowires, silicon nanoholes (RP, SNWs, SNHs), metallic nanoparticles, transparent electrodes and organic materials have been discussed which are playing significant roles in the performance enhancement of the organic/Si HSCs.

Based on these techniques and processes, it is not evident that a specific method will be considerably better than the other for organic/Si HSC device fabrication. Though, subject to the structural designs of the devices, employment of device physics, materials with proper properties, device structures, and process treatment are the parameters that play important roles in boosting the performances and yields of devices. Hence, we should recognize the specific parameters and fabrication steps that are compatible with standard silicon solar cell production processes. Moreover, parasitic optical absorption is ubiquitous in plasmonic nanostructures which could not be neglected. Consequently, across the board study and understanding is required of all these factors and parameters that vital in the design and fabrications of highly efficient and low-cost organic-silicon hybrid solar cells.

Conflicts of interest

There are no conflicts to declare.

Acknowledgment

This work is supported by NSFC under grant numbers 61875241, 11734005 and MOST under Grant Number 2017YFA0205800. Dr Weiping Wu acknowledges the support of Innovate UK (Grant Number 104013), the institutional strategic grant - Global Challenges Research Fund (GCRF), that City, University of London, receives from Research England, UK Research and Innovation (UKRI).

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