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1	Advances in nanostructured homojunction solar cells and
2	photovoltaic materials
3 4	Nisar Ali <sup>1, 3, 4</sup> *, R. Ahmed <sup>1,2**</sup> , Jing Ting Luo <sup>4,5</sup> , Mingkui Wang <sup>6</sup> , Abul Kalam <sup>7,8</sup> , Abdullah
5	G. Al-Sehemi <sup>7,8</sup> , Yong Qing Fu <sup>5***</sup>
6	
7 8	<sup>1</sup> Department of Physics, Faculty of Science, University Teknologi Malaysia, Skudai, 81310 Johor, Malaysia
9	<sup>2</sup> Centre for High Energy Physics, University of the Punjab, Quaid-e-Azam Campus, Lahore,
10 11	Pakistan <sup>3</sup> Department of Physics, GPG Jehanzeb College Saidu Sharif Swat 19130, KPK, Pakistan,
11 12 13	<sup>4</sup> Shenzhen Key Laboratory of Advanced Thin Films and Applications, College of Physics Science and Technology, Shenzhen University, 518060, People's Republic of China
14 15	<sup>5</sup> Faculty of Engineering and Environment, University of Northumbria, Newcastle upon Tyne, NE1 8ST, UK
16 17 18	<sup>6</sup> Wuhan National Laboratory for Optoelectronics, Huazhong University of Science and Technology, Wuhan, People's Republic of China <sup>7</sup> Department of Chemistry, Faculty of Science, King Khalid University, Abha 61413, P.O. Box
19	9004, Saudi Arabia.
20	<sup>8</sup> Research Center for Advanced Materials Science (RCAMS), King Khalid University, Abha
21	61413, P.O. Box 9004, Saudi Arabia.
22 23	
24	ABSTRACT
25	Recently, various materials have been explored for their potential applications in homojunction
26	solar cells, which have distinct advantages of good lattice matching at the junction interfaces
27	with minimum recombination losses of carriers. This paper presents an overview of design,
28	technique, and materials in the advanced homojunction solar cells with their latest reported
29	efficiencies. We review the development of homojunction solar cells with two-dimensional (or
30	thin film) based materials, one-dimensional materials (nanowire/nanorods/nanotube), and zero-
31	dimensional (nanodots and quantum dots) based materials. Among the thin film materials
32	explored for homojunction solar cells, we mainly focus this review on CuInS <sub>2</sub> , InGaN, and InP
33	based homojunction solar cells.
34	

1 Keywords: Homojunction Solar cell; Photovoltaic; Optical property; Thin Film; Nanowire;

2 Quantum dots;

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4	Corresponding authors: *nisar.ali@utm.my (Nisar Ali)
5	**rashidahmed@utm.my (R. Ahmed)
6	*** <u>Richard.fu@northumbria.ac.uk</u> (Richard Y.Q. Fu)
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1 **1. Introduction** 

Due to the limited supply of major energy resources (such as fossil fuels) and the impact on global warming and environmental pollution, alternative and sustainable energy resources are in great demand globally [1-4]. Photovoltaic (PV) energy is regarded as one of the largest sources for clean and green energy production and could meet the energy requirements over a longer period of time in the future [5-7]. In this regard, a variety of materials and techniques have been explored for enhancement of their efficiencies, and reduction of their costs and toxicity, etc [8, 9].

Since the adventure of 1<sup>st</sup> solar cell in 1883, two major categories of solar cells have been widely 9 explored: heterojunction and homojunction ones [10, 11]. In a homojunction solar cell, the p and 10 n-type semiconductors for window and absorbing layers are fabricated by doping the different 11 12 elements into the same material. While in a heterojunction solar cell, the window layer and absorbing layer are fabricated using different materials [12, 13]. The interfaces of 13 heterojunctions are designed from layers of dissimilar semiconductors with unequal band gaps in 14 15 order to create band offsets at the level of valence and conduction bands. However, they frequently show problems such as lattice mismatch, phase separation, electron tunneling, non-16 17 radiative recombination, and morphological defects, etc [14-17]. Whereas the homojunction solar cells are based on layers of same or similar semiconductor materials with different doping 18 levels [18], and p- and n-types are created in the same or similar materials thus generally 19 20 producing a good lattice matching.

21

The output properties of a photovoltaic device are characterized by the lattice matching, bandgap,and proper choice of the material. The bandgap has an influential impact on the output properties

such as open-circuit voltage ( $V_{oc}$ ), short circuit current ( $I_{sc}$ ), fill factor and efficiency of the solar cell. The bandgap of the material is increased as the size of the crystal or particle in the materials is decreased [19], which can be explained using a simple model to correlate the excitonic energy and the bandgap of materials with variable crystal/particle size [20]:

5

 $E_g = E_{g(\text{bulk})} + \frac{h^2 \pi^2}{2R^2} \left( \frac{1}{m_e^*} + \frac{1}{m_h^*} \right) - \frac{1.8e^2}{\epsilon R} + E_{Rydberg}$ 

6 where *h* is the Plank constant,  $m_{e}^{*}$  is the relativistic mass of electron,  $m_{h}^{*}$  is the relativistic mass 7 of hole, *e* is a charge on an electron,  $E_{rydberg}$  is the Rydberg energy, *R* is the radius of the 8 nanoparticle and  $\mathcal{E}$  is the dielectric constant of the nanoparticle.

9

Historically the homojunction solar cell has a p-i-n structured configuration proposed by Ohl in 10 1941 [21]. A homojunction solar cell based on single crystalline silicon with an efficiency of 6% 11 12 was firstly reported in 1953 [22]. There was little progress in this area until 1970s when a dramatic increase in the efficiency of up to 16 to 20% was observed for Si p-n homojunction 13 solar cells [23]. In 1977, Kazmerski et al reported copper indium selenide (CuInS<sub>2</sub>, CIS) 14 homojunction solar with an efficiency of 3.62% [24]. Different groups synthesized CIS 15 homojunction solar cells and reported efficiency values up to 11.4% between 1977-1998 [24-27]. 16 The theoretical efficiency for the CIS homojunction solar cell can be as high as 32% [28]. This 17 high value of theoretical efficiency and high stability under the illumination of sunlight make it a 18 widely studied solar cell material [29]. Recently a lot of research work has been reported to 19 20 obtain high-performance homojunction solar cells using various semiconductor materials, such as silicon, copper oxide (Cu<sub>2</sub>O), indium phosphide (InP) and tin sulphide (SnS) silver zinc tin 21 sulphide (AZTS) [30-34]. Fig. 1 shows the maximum efficiency reported so far for different 22

thin-film based homojunction solar cells. Apart from silicon, among them, indium phosphide is
found to be one of the best homojunction materials with a maximum efficiency up to 22.1%.



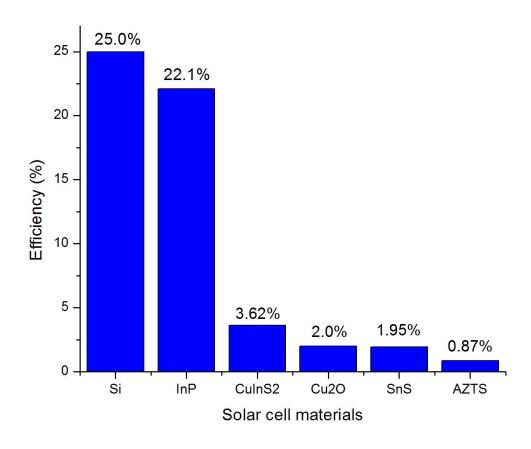
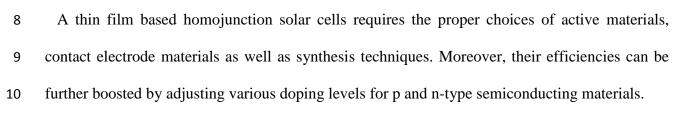


Fig. 1 Maximum efficiencies of solar cells made of different materials with a homojunction
device structure.



In this paper, we present a short review of device design, fabrication techniques and active materials employed for homojunction solar cells particularly materials including Si, CuInS<sub>2</sub>, InGaN, InP, CIGS, and Cu<sub>2</sub>O, used in homojunction photovoltaics in the form of thin films and nanostructures, which are environmentally friendly, and easy for fabrication, thus contributing to the socio-economic development.

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- 7

### 8 2. Key working mechanisms and principles of homojunction designs

9 2.1 Solar cell device with p-n, p-i-n, and n-i-p structure

A p-n junction is the fundamental building block of solar cell systems and electronic devices. 10 Homojunction solar cells can be easily made from doped and undoped intrinsic layer (i-layer) 11 incorporated into the p-n junction, thus forming either p-i-n or n-i-p structures. The idea of 12 applying an intrinsic layer in the p-n junction is to provide a buffer layer between p-n junction to 13 reduce defect densities and moderate lattice strains [35, 36]. The intrinsic layer reduces the 14 probability of exciton recombination in the absorbing layer for both p-i-n and n-i-p 15 configurations. The electric field in the depletion region separates the charge carriers, and the 16 17 minority carriers are transported to the junction through diffusion [37]. Carrier recombination is a major problem for most of the solar cells. The presence of the intrinsic layer in the solar cell 18 provide a drift assisted transport based on the mechanism that can extend electric field over the 19 whole intrinsic layer, which allows sufficient time for the carriers to be separated, thus the 20 recombination will be minimized [35]. The i-layer is frequently applied for adjustment of the 21 22 bandgap profile in the solar cell [38-40].

6

1 The p-i-n and n-i-p structures are applicable in both superstrate and substrate configurations. For example, the substrate configuration is shown in Fig. 2a, the n-i-p structure is deposited over the 2 back contact while the transparent conducting oxide (TCO) as the front contact is deposited on 3 4 the p-type layer. In a superstrate n-i-p configuration, the p-type layer is deposited on the TCO 5 coated glass while the back contact is deposited on the n-type layer as illustrated in Fig. 2c. Figs. 2b and 2d show the band offset for the p-i-n and n-i-p structures, in which an intermediate 6 7 bandgap material is sandwiched between the p-type and n-type materials [41]. Table 1 lists typical materials used in p-i-n or n-i-p homojunction solar cells. 8

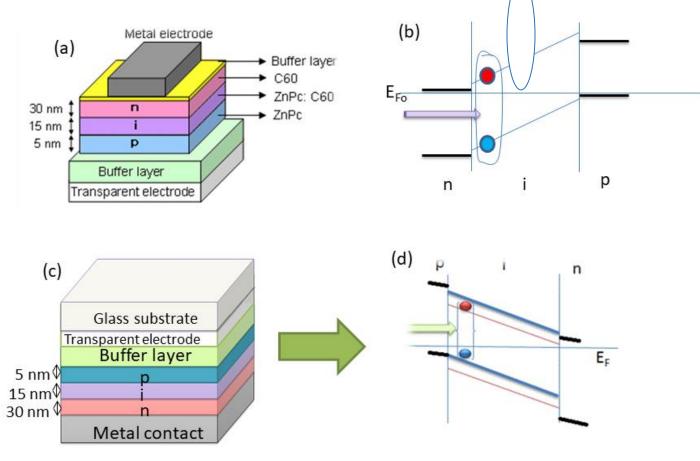


Fig. 2 The solar cells with (a) n-i-p solar cell structure, (b) the band offset in n-i-p configuration
 with hole and electron pair (c) p-i-n solar cell structure, (d) the band offset in p-i-n configuration

In literature, there are some other variations or modifications of p-i-n/n-i-p type homojunction solar cells, for example, a p-i-n solar cell with quantum wells [42], organic solar cells and quantum dot solar cells, etc., which will be discussed in the later sections.

4

5 2.2 Core-shell and axial designs

6

7 Nanowire-based homojunction solar cells generally have two types of designs, i.e., the axial and core-shell structures as shown in Figs. 3 and 4. The nanowires are generally grown using 8 physical or chemical deposition methods in which the homojunction can be created by either 9 changing the dopants in the precursor or during ambient growth conditions [43, 44]. It is possible 10 to achieve a conformal shell growth with homogeneous deposition methods at the radial surfaces 11 12 of nanowires. The arbitrary multiple shell structures can also be achieved by the successive introduction of various reactants/dopants through proper lattice structural designs, for example, 13 using single-crystalline germanium nanowires and boron-doped p-type silicon shells. Another 14 15 common approach for the core-shell design is the control of radial versus axial growth as shown in Fig. 3 The axial growth of the nanowires can be achieved with reactant additions and 16 activation at the site of the catalyst, but not on the surfaces of nanowires [45, 46]. 17

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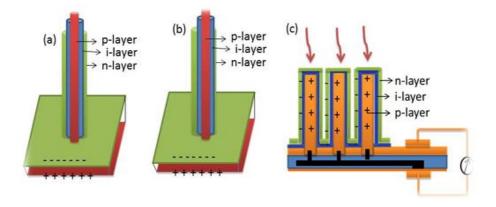
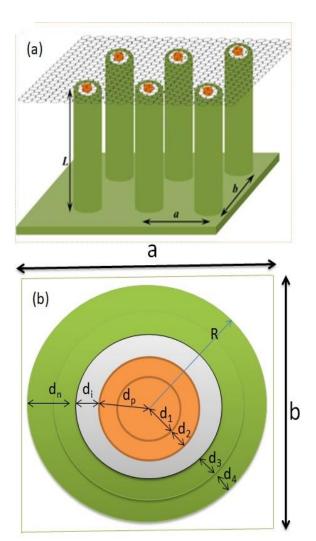


Fig. 3 Schematic cell designs: a) core-shell structure solar cell, b) axial structured nanowire solar
cell, and c) charge transport in the p-i-n structured nanowire solar cell [47].

Figure 4a is a graphene/(p-i-n) silicon nanowires (SiNWs) with the height of L and dimensions 5 of a and b, in which the external shell with green color is n-type Si, the middle shell with light 6 7 gray color is intrinsic Si and the internal core with an orange color is p-type [48]. Sunlight is 8 irradiated on the top graphene layer as shown in Fig. 4(a). Fig. 4(b) shows a cross-sectional view of the design with the single nanowire with a diameter R. Each p-i-n SiNW has a p-type core-9 10 shell with a radius of d<sub>p</sub> in an intrinsic form and a n-type outer shell with respective thicknesses 11 of d<sub>i</sub> and d<sub>n</sub>. The concentration of mobile charges are drastically decreased in the vicinity 12 positions of the p-type core and n-type shell due to the existence of an intrinsic region. 13 Therefore, space charges are formed mainly due to ionized acceptors and donors [43]. In this example, SiNW is divided into five regions [43]: i) the neutral region; ii) the depletion regions of 14 p-type Si with the width of  $d_1$  and  $d_2$ ; iii) the intrinsic Si with the width of  $d_i$ ; iv) the depletion 15 region; and v) the neutral regions of n-type Si with the width of d<sub>3</sub> and d<sub>4</sub>. In the vicinity of the p-16 type and n-type junctions with the intrinsic shell, the concentration of mobile charge is abruptly 17 changed, which creates two regions, in each of p-type and n-type regions. . 18



**Fig. 4.** G/(p-i-n)SiNWs with the height of *L* and periodicity of *a* and *b*. (a)Light is incident on graphene. The external shell of wires with green color is n-type, the middle shell with light gray color is intrinsic and the internal core with an orange color is p-type. (b) A cross-sectional view of a single nanowire with a total radius of  $R=dp+di+dn^{"}$  (Reprinted under license no. 3985140566407) [48].

# **3. Processes for homojunction solar cells**

The design toolbox for fabricating the homojunction solar cells has been extensively developed.
Various doping, diffusion, and growth processes have been applied in order to change the
intrinsic semiconductor into p-type or n-type ones, thus forming the homojunction solar cells.

5

6 There are various ways for obtaining the doped semiconductors being used as absorbing layers 7 or window layers in the solar cells, by doping the intrinsic semiconductors with various acceptor 8 or donor impurities. For all types of doping techniques particularly for silicon, ion implantation 9 is more precise, reliable, and repeatable, and allows a controlled, uniform and reproducible doping profile. Usually, the implanted species are arsenic, boron, phosphorus, boron difluoride, 10 indium, antimony, germanium, silicon, nitrogen, hydrogen, and helium, etc. [49]. For example, 11 12 Milési et al reported that using ion implantation techniques for doping, the efficiency of Si solar cells is 20.33% compared to those made using the conventional gas diffusion method (19.8%) 13 [50]. For ion implantation, the sources may be in the form of gas or solid, and heating filament of 14 15 microwave energy transforms the source material into plasma ions, which are then accelerated for implantation to transform the intrinsic semiconductors into the extrinsic ones [51]. The ion 16 implantation process can be used for both amorphous and crystalline materials. The ion energy 17 requirement for ion implanter varies from sub-keV to more than 3 MeV. For ion implantation, 18 the projected depth of ions depends not only on the energy of the ion but also on the density of 19 20 the material, the nature of ions and the gas pressure [52]. The process parameters, such as depth of the desired dopant and concentration of dopants, etc. are quantified directly in the apparatus 21 22 settings for implantation of dose and energy [52]. However, the ion implantation produces lattice 23 disorders because of the high energy carried out by the dopant. Although it is possible to relieve

this lattice disorder due to the energetic ions by using post-annealing, it is impossible to toally
remove the lattice disorder effects created by high energy ion implantation [53].

3

For compound semiconductors, solution method and gas-phase techniques are generally used for 4 doping. For example, the aqueous solution method operated at a high temperature is used for 5 doping of Al-ZnO, Cl-ZnO, F-SnO2, Ga-ZnO, etc. using the aqueous solution methods [54, 55]. 6 Copper indium gallium sulphide (CIGS) homojunction solar cell has been reported to fabricate 7 using the solution treatment technique. The post-annealing step at a suitable temperature is often 8 9 used to quantify the functionality of dopants inside the parent material [56]. The dopant concentration can be controlled either with the concentration of dopant salt in the solution or 10 with the kinetics of the dopant in the bath. The gas phase diffusion techniques activate the 11 12 impurities at a high temperature to diffuse the impurities into the substrates and create a shallow junction. Impurity diffusion at a high temperature of 800-1100 °C is commonly carried out in a 13 furnace to form either n or p-type of semiconductors [57]. Alexandra et al. [58] reported Zn 14 15 doping in InAs via the gas phase technique for p-InAs. Harry et al. [59] reported the doping of Si in GaAs for p-type silicon to form a homojunction solar cell. Steele et al. [60, 61], Nowotny et 16 al. [62], Lane and Kilner [63] also reported to use the gas phase diffusion for doping to form 17 various types of homojunction solar cells. 18

19

There are a few other commonly used methods such as rapid thermal annealing (RTA), which are usually performed at a high temperature around ~1100°C for a shorter time such as a few seconds followed by quenching [64, 65]. Tang et al. [66] reported the growth of solution-

- 1 processed core-shell CdS nanowires in a quartz tube on gold loaded catalyst by rapid thermal
- 2 annealing on silicon substrate carried out at 800°C in the argon gas flow [64, 66].
- **Table 1** Typical materials used in p-n, p-i-n or n-i-p homojunction solar cells

Semiconductor materials	Р	Ι	N	Ref.
Si	p-type Si (doped Si with Boron)	Amorphous Si, or not heavily doped Si	n-type Si (doped with Arsenic)	[67]
CIGS	p-CIGS (CIGS is a p-type semiconductor material)	i-ZnO	n-CIGS (The CIGS film was immersed in 0.8mM CdSO <sub>4</sub> +1.5M NH <sub>4</sub> OH solution heated for 22 minutes at 80°C)	[68, 69]
InGaN	p-InGaN (The variation in In and Ga concentration will lead to p- type InGaN. If In/Ga =0.53, it will lead to p-type material))	i- InGaN	n- InGaN (When the In/Ga ratio is greater than 0.53, it will lead to n- type material)	[70]
InP	p-InP (By proton bombardment with 1.9x10 <sup>17</sup> cm <sup>-3</sup> p dopants)	i-InP	n-InP (By proton bombardment with 1.2x10 <sup>17</sup> cm <sup>-3</sup> n dopants)	[71]

# 7 4. Commonly used materials for homojunction solar cells

Recently, various materials at different dimensional scales have been explored to make highperformance homojunction solar cells, including 1) two-dimensional materials; 2) onedimensional materials such as nanowire/nanorods/nanotube; and 3) zero-dimensional materials
such as nanodots and quantum dots.

# **4.1 Thin film based homojunction solar cells**

**4.1.1 Cu<sub>2</sub>O homojunction solar cells** 

1 Cuprous oxide (Cu<sub>2</sub>O) homojunction solar cells have attracted considerable attention because 2 the  $Cu_2O$  shows p-type conductance, high absorption coefficient, low energy bandgap of about 1.2 eV, low fabrication costs along with its low cost, abundance availability and non-toxic 3 nature. The theoretical bandgap obtained using the first principles approach is predicted to be 1.8 4 eV, which is much higher than the experimental value of 1.2 eV [72-74]. The n-type counterpart 5 6 of the homojunction solar cell is cupric oxide (CuO) which is more thermally stable than  $Cu_2O$ . 7 For example, below 400 °C, the surface of Cu<sub>2</sub>O is chemically unstable compared to CuO [74-76]. Minami et al. have reported an efficiency of 5.38% of the Cu<sub>2</sub>O from experimental work, 8 9 however, the theoretical conversion efficiency is predicted to be 20% [77]. This limit is mainly due to the lack of deposition techniques for the production of high performance n-type Cu<sub>2</sub>O 10 solar cells [78]. The p-type conductivity is typically introduced due to the presence of copper 11 12 vacancies in the cuprous oxide. Recently there was a report on the synthesis of n-type  $Cu_2O$ using an electrodeposition method in an aqueous solution, for fabricating the p-n junction 13 homojunction Cu<sub>2</sub>O solar cells [79]. High-quality interfaces, grains orientations, and textured 14 15 surfaces were all found to improve the photovoltaic properties (e.g. efficiency) of Cu<sub>2</sub>O based homojunction solar cell [80-82]. The enhancement in photovoltaic efficiency can also be 16 achieved by controlling grain orientation and surface microstructure [80] or using a textured 17 material which may increase the absorbance of the solar spectrum by increasing the reflections 18 [83]. McShane et al. fabricated Cu<sub>2</sub>O homojunction solar cells with an efficiency of 0.29% by 19 20 electrochemical deposition of p-Cu<sub>2</sub>O/n-CuO layer [84, 85]. Han and Tao employed a two-step electrochemical deposition technique to fabricate the Cu<sub>2</sub>O homojunction solar cells and 21 obtained an efficiency of 0.1% [76]. Similarly, Colleen et al. reported a cuprous oxide 22

homojunction solar cell with an efficiency of 1.06 %, V<sub>oc</sub> of 0.621 V, fill factor of 44% and I<sub>sc</sub> of
4.07 mA [76, 86, 87].

3

4

#### 4.1.2 CulnS<sub>2</sub> thin-film homojunction solar cells

5

6 CuInS<sub>2</sub> is a chalcopyrite semiconductor which has been intensively studied as low-cost terrestrial 7 photovoltaics. Its direct bandgap energy (1.55 eV) is near to the optimum bandgap value for an efficient conversion rate of solar energy into electrical energy. It is also considered an efficient 8 9 material for a solar cell with minimum losses inside the cell, thus it could play a crucial role in reducing the manufacturing cost of photovoltaic cell at a large-scale production [88]. In 1998 10 Kazmerski and Sanborn reported the fabrication of the CIS homojunction solar cell with 3.62% 11 12 efficiency [24]. No further new result is found in literature for the updated efficiency of CIS solar cell. However its theoretical efficiency is 28%, which is too high if compared with the 13 experimental values [24]. 14

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- 16 **4.1.3 InGaN homojunction solar cell**
- 17

InGaN is a direct bandgap material which has been frequently used as a homojunction solar cell. It has been reported with variable bandgap values from 0.65 to 3.4 eV by simply changing the material's composition [81, 82, 84]. It has many advantages such as strong exciton binding energy, large oscillator strength, and natural waveguiding effect. The InGaN was reported to have a broad spectral response within the wavelengths from 456 nm to 600 nm with a reduced stacking fault density [89]. Moreover, InGaN has a high absorption coefficient of almost 10<sup>5</sup>

cm<sup>-1</sup> near the band edge, which enhances its absorbance such that most of the incident photons 1 2 are absorbed in a few hundred nanometers into this material [82, 87, 90-92]. All these could improve its photovoltaic properties e.g. low effective mass, high carrier concentration, superior 3 electrical properties, high radiation, and temperature resistance, etc. [93]. For example, Wang et 4 al. [94] reported an open-circuit voltage of 0.43 V for the homo-junction InGaN solar cell, which 5 is much smaller than the energy band gap value. The absorption region of the InGaN could be 6 extended using the idea of p-i-n structured homojunction solar cells as compared to 7 heterojunction solar cells [95-97]. 8

9

For the InGaN-based tandem homojunction solar cell, it is necessary to alloying InGaN with 10 varying concentrations of In, Ga and N [98, 99]. The Ga-rich InGaN films were prepared to 11 study the effect of composition effect and also to reduce the lattice mismatch. The InGaN-based 12 13 homojunction solar cells can be made using the metal-organic vapor phase epitaxy (MOVPE) or 14 molecular beam epitaxy (MBE) technique by changing the gas concentration during the deposition process [99, 100]. The MOVPE grown InGaN homojunction solar cell showed a 15 maximum efficiency of 18% of In content in the compound [101]. Misra et al. [102] obtained the 16  $In_{0.31}Ga_{0.69}N$  homojunction solar cells grown using the MBE With an  $I_{sc} = 1.99$  mA/cm<sup>2</sup> and 17 V<sub>oc</sub>=0.78 V. Jani et al. [95] and Neufeld et al. [103] developed GaN p-i-n structured and InGaN 18 p-i-n structured devices with 43% and 63% external quantum efficiencies (EQEs), respectively 19 [104]. Chen et al. [105] also reported InGaN homojunction solar cells based on a p-i-n structure, 20 with the values of  $V_{oc}=2.5$  V and fill factor=61%. However, the defects in the InGaN were found 21 to cause a large leakage current in the device structure that makes it difficult to measure the turn-22 on voltage and output power [99]. By lowering the In content in the compound, a p-i-n structured 23

InGaN solar cell was developed with high value of V<sub>oc</sub> and I<sub>sc</sub> and fill factor [99]. The p-type
polarity of InGaN on a sapphire substrate was also achieved by Mg doping for homojunction
solar cell with good electrical and optical properties [105].

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4.1.4 InP homojunction solar cells

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Indium phosphide (InP) is one of the promising materials for high conversion efficiency solar cells. The conversion efficiency of ~ 23%, near to GaAs solar cells, was predicted for InP solar cells under the air mass zero (AMO) illumination [105]. The InP solar cells have exhibited good characteristics including sinterability at a fairly low temperature (below 120°C), a high forward bias under a minority carrier injection, and a p-type nature with increased dopants [61]. For these reasons, the InP shows its tremendous potential in developing good homojunction solar cells with a high efficiency [106].

14

Yamamoto et al. reported the fabrication of InP homojunction solar cells with a conversion 15 efficiency 16.5% [107, 108], and showed that the InP solar cells had a higher resistance to 16 radiation degradation (1 MeV electron and 10 MeV proton irradiation) than those of the Si and 17 GaAs solar cells [61]. Through theoretical simulation results, the optoelectronic properties of the 18 19 InP could be significantly improved with a much better with a long-term stability of the photovoltaic power and high radiation tolerance [109]. Currently, the InP-based homojunction 20 solar cells have few reported efficiency values due to issues such as surface recombination [110], 21 22 but these can be sufficiently controlled through the p-i-n structured InP homojunction solar cells 23 [111].

#### 2 4.2 Nanowire and nanoparticle-based homojunction solar cells

3

Nanowire-based solar cells have potential advantages over conventional thin-film solar cells
because of their improved characteristics including photoconversion efficiency, reduced light
reflections, improved bandgap engineering, and light trapping, facile strain relaxation, etc [47].
Moreover, the associated low material cost and improved quality of the materials show
promising results.

9

10 A p-n junction must be introduced in a homojunction nanowire for charge separation and collection as shown in Fig. 3a [112, 113]. Bacaksiz et al. fabricated a p-n homojunction solar cell 11 12 on a glass substrate using n-type of ZnO nanorods prepared using spray pyrolysis technique, followed by the deposition of a p-type ZnO outside of the nanorod layer. They concluded that the 13 series resistance and changes in the diffusion barrier energy are attributed to the observed p-n 14 15 homojunction behavior of the ZnO nanowire. Very low barrier energy (0.122 eV) was reported for ZnO nanorod homojunction solar cells [114, 115]. Sun et al. [116] prepared the ZnO 16 17 homojunction nanowires using a hydrothermal method, and they observed an n-type conductivity in the ZnO nanowires due to oxygen vacancies and p-type conductivity in the oxygen-rich ZnO. 18 In this process, the n-type ZnO was served as a template for the p-type ZnO, and hence a single 19 20 ZnO nanowire p-n homojunction solar cell was obtained [117]. Yang et al. reported a p-type conductivity of ZnO doped with Na via magnetron sputtering [118]. They found that doping of 21 Na in the ZnO increased the hole concentration up to  $10^{16}$ - $10^{18}$  cm<sup>-3</sup>, which were further changed 22 23 with post-annealing, changes of growth temperatures and Na contents in the target [119]. The theoretical calculation was also used to predict the p-type conductivity in ZnO with potassium (K) doping [120]. P-type conductivity for K:ZnO was also reported by Tay et al. [120], with a hole concentration of 3.8×10<sup>17</sup>cm<sup>-3</sup>, indicating that the p-type conductivity can be easily produced to make a homojunction ZnO solar cell.

5

Li and Zhao reported a solar cell made of  $\alpha$  and  $\beta$ -Bi<sub>2</sub>O<sub>3</sub> nanowires, and less than 5% lattice 6 7 mismatch was achieved for the  $\alpha/\beta$ -Bi<sub>2</sub>O<sub>3</sub> homojunction photocatalyst [121]. Yue et al. reported 8 a solar cell made of SnS homojunction nanowires on an aluminum substrate with gold nanoparticles used as the catalyst, and obtained the short circuit current density and energy 9 conversion efficiency of 7.64 mA cm<sup>-2</sup> and 1.95%; and open-circuit voltage and fill factor values 10 of 0.65 V and 39% respectively [44]. Homojunction solar cells were also made using TiO<sub>2</sub> 11 12 nanoparticles with anatase and rutile phases (to form a p-n homojunction), thus creating efficient surface-phase junctions [122, 123]. For the homojunction solar cells made of  $p-Ga_2O_3$  and n-13 Ga<sub>2</sub>O<sub>3</sub> nanowires [124] the charge separation phenomena in the p-n homojunction were found to 14 15 be significantly enhanced by the inner electric field [125, 126].

16

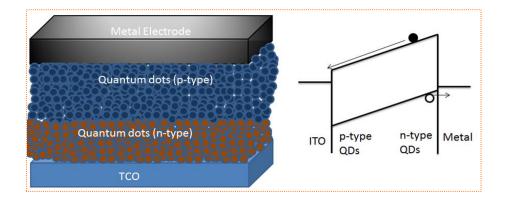
## 17 4.3 Quantum dots/wells homojunction solar cell

18

The monodispersed and high-quality quantum dots (QDs) and quantum wells (QWs) could result in remarkable improvement in charge recombination and carrier trapping. Recently significant development has been achieved in the p-n homojunction QD solar cells, with improved  $V_{oc}$  and stability in these solar cells, which were mainly attributed to the solid-state ligand exchange and ligand effect due to the properties of QDs [127]. In order to form a p-n homojunction using the QDs, the thick electron acceptor layer (TiO<sub>2</sub> or ZnO) in a conventional solar cell can be replaced
by an n-type QD layer which allows the p-n junction to receive light from both the ends, as
illustrated in Fig. 5.

4

There were a lot of reports about the electrical characterization of homojunction QD solar cells. 5 For example, Wang et al reported a QD homojunction solar cell of TiO<sub>2</sub> with stacking different 6 7 layers, which have two-layered TiO2 nanoparticle electrodes, three layered TiO2 nanoparticle 8 electrodes, and five layered TiO2 nanoparticle electrodes [128, 129].Results showed that the short-circuit current density for 5 stacked layer (14.4 mA cm<sup>-2</sup>) was higher than that of the 1-9 stacked layer (9.6 mA cm<sup>-2</sup>), thus leading 5.1% efficiency for the former solar cell. Ning et al. 10 11 reported an efficiency of 6.6% for the homojunction PbS QD solar cells although it is still lower 12 than those reported for the heterojunction solar cells [9].





14 **Fig. 5** p-n homojunction quantum dot solar cell and its band structure.

1 The ligands on the QDs were reported to play a vital role in enhancing the overall performance 2 of the solar cells [124]. The optoelectronic properties of the QDs are related to the separations 3 between the QDs and hence interparticle interactions. Murphy et al. reported that the ligand in an oleic acid could reduce the distance of the PbS QDs from 1.8 nm to 0.4 nm in aniline [130]. The 4 small separation between the QDs could effectively couple them electronically thus leading to a 5 6 dramatic decrease in the resistance and changes in the conductivity type of the ODs. These are 7 the major breakthroughs toward the advancement of QDs homojunction solar cell [131]. For example, Sargent et al. reported a PbS homojunction QD solar cell with 7% efficiency [132]. 8 9 Accordingly, the compatibility of different solvents has been explored, and the ligand exchanges and thiols, halogens, or combinations of passivants are proven to be effective for the solar cells, 10 mainly because the QDs yield a complex surface structure [133]. Future research should be 11 12 focused not only on ligand exchange solvents, but also on multi-electron generation in a variety of shapes, compositions, and structures for the quantum structure solar cell devices. The 13 combination of proper passivation solutions and multiple exciton generations (MEG) in the 14 15 homojunction QD solar cells will increase their efficiency in the near future.

16

## 17 4.4 Organic homojunction solar cells

18

Organic solar cells have attracted enormous attention due to the availability of abundant raw materials, ease of fabrication and light-weight. Heliatek Company recently reported a new world record efficiency of 13.2% for the organic solar cells. Fig. 6 shows the structure of an organic homojunction solar cell in a p-i-n configuration with i-layer composed of n-type and p-type organic semiconductor material. The ionized donor and acceptors in the n-type and p-type

1 semiconductors compensate each other while the co-deposited interlayer serves as an intrinsic 2 semiconductor layer, and the built-in potential is distributed across the i-layer, similar to those of the p-i-n structured amorphous silicon solar cells [134, 135]. Nelson et al. [136] reported an 3 4 efficiency of 2.4% for a homojunction p-i-n structured polymer solar cell [136]. Hiramoto et al. reported the changes in conductivity types from n-type to p-type of perylene pigment upon Br<sub>2</sub>-5 doping [134]. A p-n homojunction solar cell using  $C_{60}$  films and pervlene pigments was 6 fabricated and achieved parameters of J<sub>sc</sub> of 3.0 mA cm<sup>-2</sup>, V<sub>oc</sub> of 1.69 V, FF of 0.47, and an 7 efficiency of 2.4% [134]. Kubo et al. reported p-n homojunction solar cells fabricated using 8 phase-separated co-deposited films through doping processes [137] with a simultaneously doping 9 strategy, which allows the formation of a metal-free p-n homojunction solar cell of 0.5 µm thick. 10 This has been applied to achieve a 0.3 µm minority carrier diffusion length, thus leading to the 11 12 suppression of the interfacial recombinations and thus an efficient solar cell [137]. The high short circuit density and open-circuit voltage have been achieved due to the usage of low 13 bandgap materials with highest occupied molecular orbital level. 14

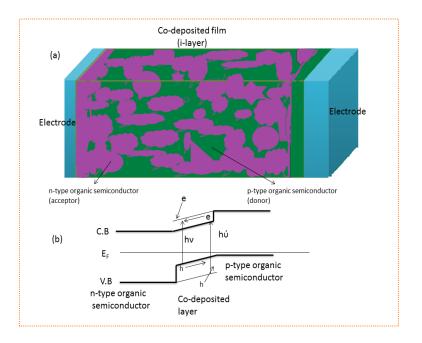




Fig. 6 a) Co-deposited p-i-n structured solar cell. An i-layer co-deposited with n- and p-type
semiconductors is sandwiched between respective p- and n-type layers. b) Band structure of the
p-i-n structured solar cell.

#### 6 5. Conclusions and future outlooks

7

This paper presents a concise review of the advances in homojunction solar cells based on thin films, nanostructured and organic materials. The thin film based homojunction solar cell designs could not only minimize the material usage, but also reduce the material dimensions. For thinfilm homojunction, solar cells, the Cu<sub>2</sub>O, CuInS<sub>2</sub>, InGaN, and InP materials were recently investigated extensively worldwide [138]. The gradual increase in the efficiency and other parameters related to solar cells for the materials have been discussed in this paper. The maximum efficiency was found to be 16.5% for InP homojunction thin-film solar cells compared

1	to 44.5% for heterojunction solar cells. Nanowires and quantum dots were found to have better
2	potentials for homojunction solar cells due to good optical and electrical properties, effective
3	charge separation mechanisms and low cost. Some materials e.g. cadmium in CdTe, arsenide in
4	GaAs, and selenium in CdSe or ZnSe were reported to be toxic, thus they are suggested to be
5	used with a great care [35]. The nontoxic nature of Cu <sub>2</sub> O, InP, Si, CIS, and InGaN was reported
6	by different groups and has been verified by the material safety data sheet (MSDS) [139-141].
7	The non-toxic and homojunction characteristics of the discussed materials will show their
8	advantages for their future applications. Their efficiency, I-V characteristics and recombination
9	processes and fabrication techniques have been widely investigated.
10	To further improve the performance of the homojunction solar cells, the following directions
11	should be considered:
12	1. Improvement in synthesis techniques and advanced characterization techniques are
13	required for quantitative and qualitative analysis.
14	2. Optimizing the Fermi levels and the conductivity of the p and n-type layers to maintain
15	ideal ohmic junctions.
16	3. The search for new cheap and nontoxic materials with dual conductivity for the
17	fabrication of homojunction solar cell.
18	The surface interface recombination and surface roughness, doping control, scalability, and
19	rapid scaling, stability, integration into module and device packing are few challenges in
20	photovoltaic technology. One of the constraints of a homojunction solar cell is that the active
21	absorbing layer must be near the junction in order to minimize the absorption losses. It is
22	anticipated that the issue can be addressed using thin absorber layer structure in the
23	homojunction solar cell.

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- 10

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