Chapter 7

Hybrid Materials for Solar Cells

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Abstract

Solar energy is an attractive renewable energy source across the globe that can help overcome the energy crises and has the ability to replace conventional resources. Hybrid solar cells have higher conversion efficiency. In the current chapter the research related to the carbon nanotubes, organic and inorganic solar cell, dye-sensitized solar cells and tandem solar cells are reviewed. The organic solar cells are most suitable and economic, but it has low efficiency of up to 15%. The inorganic solar cells are very expensive and have high efficiency of up to 46% and are used in space applications. The hybrid solar cell is the third type and the perovskite tandem has already proven to be quite efficient (17%) and low cost, mostly because of the cheap materials that are being used.

Keywords

Renewable Energy, Hybrid Solar Cell, Carbon Nanotube, Organic and Inorganic Solar Cell, Dye Sensitized Solar Cell, Tandem Solar Cell

Contents

Hybrid Materials for Solar Cells	149
1. Introduction.....	150
2. Types of hybrid cell based on material used in it	151
2.1 Carbon nanotubes (CNTs)	151
2.2 Organic-inorganic solar cell	154
2.3 Dye sensitized solar cells.....	160

2.4 Tandem solar cells	164
Conclusion.....	168
References	168

1. Introduction

Cost-effective and environmentally sustainable renewable energy generation remains a major challenge for both technological and scientific development [1-3]. Solar energy will be a significant contributor to future energy production[4,5].Solar power is clean, renewable and sustainable since no carbon dioxide is produced [6]. In order to be a huge energy source to compete with fossil fuels, the cost of producing solar cells must still be reduced. The effort to create new materials for solar cells has been difficult, and recently new classes of photovoltaic materials have been discovered. The hybrid solar cell is one of the latest most commonly produced photovoltaic(PV) cells [5]. The introduction of a combination of polymers and nanoparticles in cell designs is rapidly replacing silicon PV modules to increase efficiency and reduce the cost of PV systems[7].

PV cell development is traditionally split into 3 generations. The first generation is the era of crystalline silicon cells. Second is the thin-film solar cells generation and in the third PV generation, concentrating photovoltaic (CPV), dye-sensitized solar cells (DSSC), organic-inorganic hybrid solar cells, perovskites etc. are beginning and has yet to be commercialized to an extent [8]. CPV has the capability of having the highest performance of any PV module, though it is not clear at what value. Other organic or hybrid organic/traditional (DSSC) PV technologies are at the research and development (R&D) stage [9]. These offer lower performance, but also lower costs and weights, and offer free-form sizes; thus could fill the market [10].

The attributes of organic as well as inorganic semiconductors are incorporated into hybrid solar cells. Photovoltaics are hybrids with organic material consisting of conjugated polymers which absorb the light and act as an electron donor. The acceptor and transporter in the hybrid solar cells are the inorganic materials [11,12]. Innovation is being shown in the use of carbon nanotubes (CNTs) in PV systems. Because of their unique tubular structures and dimensions, carbon nanotubes exhibit attractive mechanical and electronic properties[13].Transparent conduction electrodes made from CNTs are a fine substitute for indium-tin-oxide electrodes. Charges in the carbon nanotubes help to improve the carrier's mobility and conductivity so that the recombining of photo-generated charge improve the photovoltaic effect[14,15].

The dye-sensitive solar cells as high energy performance and low-cost material have been taken into consideration in recent years[4,16]. The research activity on solar cells, organic-inorganic photovoltaic devices has increased exponentially, especially since the discovery of the dye-sensitive nanocrystalline solar cell. A new record-breaking conversion performance of 11 % has already been reached, but its practicality remains difficult in the electrolyte instability[15,17–19].

Tandem solar cells use a large bandgap material as a front cell and a small bandgap material as a rear cell to minimize excess thermal energy [20,21]. In this chapter, we have discussed and reviewed hybrid material for solar cells consisting of carbon nanotubes, DSSC, hybrid organic–inorganic solar cells, polymer-nanoparticle composite-based solar cells, etc.

2. Types of hybrid cell based on material used in it

2.1 Carbon nanotubes (CNTs)

Metal decorated carbon nanotubes have multi uses such as exciton carrier within a polymer-based photovoltaic layer and semiconducting CNT as the photoactive layer[14,22–24]. The CNTs in donor and acceptor form photovoltaic systems have been developed with functionalized multiwalled carbon nanotubes by Pradhan and co-workers [25], and also developed the heterostructure devices between composite polymer CNT and buckminsterfullerene or preferably C₆₀ layers. CNTs in the CNT/C₆₀ polymer framework produced a greater volume of exciton dissociation and increased mobility for carrier transport [25].

Somani and co-workers [26] presented Platinum nanoparticles in organic/organic-inorganic n-Si/poly (3-octylthiophene) (P3OT/n-Si) hybrid solar cell (HSC) in a photovoltaic application (Figure 1) [26]. They found that a multi-wall carbon nanotube with platinum (MWCNT-Pt) is a better contender than pristine MWCNT for inclusion in P3OT/n-Si heterojunction solar cells to improve their efficiency. Conversion efficiency with MWCNT-Pt = 0.775% while in MWCN conversion efficiency = 0.145% [27].

By using a Pt nanoparticles-adsorbed carbon nanotube yarn as a counter electrode, Zhang et al. [28] have obtained 4.85% power conversion efficiency with normal illumination (AM1.5, 100 mW / cm²) (Figure 2) [28]. According to the authors platinum (Pt) nanoparticles adsorbing in a porous nanotube yarn results in the increased interfacial region of Pt/electrolyte and significantly reduces the resistance of charging movement across the electrolyte interface. It was proposed that such yarns could minimize the use of

noble metals, reduce the weight of the equipment and improve the efficiency of the solar cells.

Figure 1 P3OT/n-Si solar cell (Reprinted with the reference Somani et. al., 2008, permission of AIP Publishing)

Figure 2 Illustration of the preparation processes of Pt-adsorbed hybrid yarns and application as counter electrodes for fibre solar cells. (Reprinted from the reference [28], Copyright ACS)

MWCNT hybrid is synthesized by Arbab et al. [29] as an activated carbon (AC)-doped composite electrode (CE) for quasi-solid state solar cells with dye sensitization (DSSCs) (Figure 3) [29]. The MWCNTs model, with AC-doped, displayed a considerable improvement in electrocatalytic (ECA) activities towards electrolyte polymer gel, which demonstrated a strong mechanism for electron transportation. An inappropriate amount of quasi-solid electrolyte may be caused by inadequate oxygen surface groups and defect rich structure, and multiple locations to catalytic iodide/triiodide reactions. The

corresponding DSSC compound of this counter electrode was 10.05% effective with a large fill factor (83%)(Figure 4)[29].

Figure 3 AC-doped MWCNT based DSSCs. (Reprinted from the reference [29], Copyright ACS)

Figure 4 Photocurrent generation in DSSCs. (Reprinted from the reference [29], Copyright ACS).

2.2 Organic-inorganic solar cell

The hybrid solar cell is considered to be a viable alternative to low-cost photovoltaic devices, as Schottky junctions could be formed in an organic and inorganic matter [30]. The production of hybrid solar cell structures has been carried out through inorganic materials including quantum dots, nanoparticles and nanowires [31–36].

High-strength conversion efficiency has been demonstrated by Yodying Yong et al. [37] in inorganic-organic solar cells encapsulating titanium dioxide (TiO_2) filled with poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl C61-butyric acid methyl ester (P3HT/PCBM) as the active layer. An open-circuit voltage, short-circuit current density, fill factor and power conversion efficiency of the high-grid solar cell, respectively, is 646mV, 9.95mAcm^{-2} , 51.6% and 3.32%[37].

Balis and coworkers[38]made a cell by combining nc- TiO_2 , P3HT and cadmium sulfide (CdS) quantum dots, in the presence of 2-amino-1-methylbenzimidazole (AMBI) with an efficiency that reached $0.87\pm 0.13\%$. Cells exhibited amazing stability and power conversion efficiency [38].

Jayan and Manthiram [39]have shown the performance and stability of P3HT- TiO_2 -based cells (Figure 5) [39] can be improved by using copper (Cu) as the top hole collecting electrode in the absence of oxygen (Figure 6) [39]. These results can contribute to the synergy of hybrid solar cell stability. This research nevertheless reflects a preliminary study of the Cu effect on the stability of hybrid solar cells with P3HT- TiO_2 in an inert atmosphere [39].

Figure 5 Interfacial prototype of P3HT- TiO_2 solar cell. (Reprinted with permission from reference [39], 2011 Copyright ACS).

Figure 6 Energy band diagram of P3HT-TiO₂. (Reprinted with permission from reference [39], 2011 Copyright ACS).

Sequential hybridized polymer solar cells are fabricated by Liao and co-workers[40](2012) using a rutile TiO₂ nanoarchitecture array. The diotic molecule plays an important role in the interface morphology of the TiO₂ nanorod (NR)/P3HT hybrid, becoming a photocurrent contributor. *cis*-Ru(H₂dcbpy)(dnpbpy)(NCS)₂(Z907) and Indoline dye (D149) dye molecules not only provide proper band alignment between P3HT/TiO₂NR, but also improve the consistency of the hybridized interface morphology. Three-dimensional TiO₂ nanodendrite (ND) arrays have been further assigned to expand the interface area of the planned heterojunction hybrid solar cell. A remarkable efficiency of 3.12% is found in the D149-modified TiO₂ ND array/P3HT hybrid solar cell [40].

Almohsin and Cui [41] investigated a graphene-enriched P3HT (G-P3HT) and porphyrin grafting of the zinc oxide (ZnO) NW hybrid structure for applications in the solar cell which significantly improves the cell efficiency. According to their study, the cell efficiency increases from 0.09 to 0.4%. Using modified porphyrin which is responsible for improved charge injection and increased light absorption at the junction interface(Figure 7) [41]. This study shows that hybrid structures have promising applications for fabricating high-efficiency solar cells [41].

Greaney and coworkers [42] fabricated P3HT: CdSe-(tBT) hybrid solar cells devices revealed efficiencies of 1.9% and a maximum open-circuit voltage (V_{oc})=0.80 V. The open-circuit potential associated with devices using the cadmium selenide (CdSe) tert-Butylthiol (tBT) acceptors is recognized by lowest unoccupied molecular orbital

(LUMO) and highest occupied molecular orbital (HOMO) energy of P3HT. The authors showed a direct relationship between the LUMO energy displacement induced by the ligand and the open circuit potential observed in functional electrical cells [42].

Figure 7 Schematic diagram (a) energy charge transfer (b). (Adapted from reference [41], 2012. Copyright ACS).

Jeong et al. [43] revealed the Si nanocones and poly (3, 4-ethylenedioxythiophene): polystyrenesulfonate (PEDOT:PSS) hybrid solar cell as conductive polymer (Figure 8) [43]. Nanocones arrangement with an aspect ratio of less than two tailored structures for enhancing the absorption of light, and providing excellent antireflection and light diffusion results. The efficiency of power conversion above 11%, the optimum nanoconic structures for the thickness of 10 μm , if the Solar Cell has a short-circuit current density of up to 39.1 mA/cm^2 (Figure 8b). Hybrid Si nanocone/PEDOT: PSS solar cells are promising as a cost-effective alternative solution to the process with a very thin material [43].

Figure 8(a) Fabricated Si nanocone/polymer solar cell. (b) Characteristics of Si nanocones coated with PEDOT: PSS and Au grid. (Adapted from reference [43], 2012 Copyright ACS).

Pudasaini et al. [30] described hybrid solar cell device SiNP/PEDOT: PSS. power conversion efficiency (PCE) was found to be 9.65%. With the use of the ultrathin atomic layer deposition (ALD) deposited aluminum oxide (Al_2O_3) junction activation layer (Figure 9) [30], the short-circuit current density, open-circuit voltage, PCE value and fill factor were observed to be $30.1\text{mA}/\text{cm}^2$ and 578mV , 10.56%, 71% respectively [30].

Figure 9 (a) Schematic illustration of the fabricated SiNP/PEDOT: PSS solar cell. (b) Chemical structure of PEDOT: PSS. (Reprinted with permission from reference [30], 2013 Copyright ACS).

Eom et al. [44] first, inverted bilayer HSC of $\text{ZnO}:\text{P3HT}$ IMs, ZnO act as n-type semiconductor and in second, inverted BHJ solar cell of $\text{ZnO}/\text{P3HT}:\text{PCBM}$, it roles as an electron transport layer/hole blocking layer(ETL/HBL). After the interfacial modification in the $\text{ZnO}:\text{P3HT}$ bilayer device (Figure 10) [44], and $\text{ZnO}/\text{P3HT}:\text{PCBM}$ based bulk heterojunction (BHJ) device, with the efficiency of 0.42% and 4.69% is achieved, respectively. The authors found that IM's help to reduce recharge and leakage by reducing the number of defect locations and trap and improving hydrophilic ZnO [44].

Qin et al. [45] reported graphene quantum dots with bright blue emission and showed a slight difference in the carrier band between TiO_2 and P3HT. This bulk heterojunction of high-energy photons increased the peak by incorporating graphene quantum dots (GQDs) into the hybrid heterojunction as an additional buffer layer. This intense mix gave 3.16% more PCE, than traditional $\text{TiO}_2/\text{P3HT}$ devices. GQDs unique band structure funnels a photoexcited charge carrier directly into the circuit. Although this function is far from optimized, it offers profound advantages, as well as the relative ease of electronic

structures, low toxicity, and promising candidate buffer material for scalable photovoltaic applications [45].

Figure 10 The basic device structures of hybrid solar cells in this study: (a) ZnO:P3HT bilayer structure and (b) P3HT:PCBM BHJ structure with ZnO as ETL/HBL. (adapted from reference [44], 2014, permission ACS).

Lee and co-workers [46] demonstrated a high-performance Si-organic hybrid heterojunction solar cell utilizing TiO_2 interlayer between PEDOT:PSS and Si nanoholes to produce a conformal contact on the surface of the Si nanostructure. The high $V_{oc}=0.63\text{V}$ was attributed to the surface passivation of silicon (Si) by annealed TiO_2 , with this value of $J_{sc}=35.7\text{mA}/\text{cm}^2$ and $\text{PCE}=14.7\%$ were obtained. Authors convinced that with proven surface passivation and conformal PEDOT: PSS/Si nanohole interfaces for enhanced contact, this Si-organic hybrid heterojunction solar cell with solution-processed TiO_2 interlayers has excellent potential for application as a high-efficiency and low-cost Si solar cell [46].

Um and co-researchers [47] demonstrated an silver/silicon dioxide (Ag/SiO_2) electrode embedded Si substrate cells (Figure 11) [47]. With a 607mV open-circuit voltage and a $34.0\text{mA}/\text{cm}^2$ short-circuit current density; the 1cm^2 solar hybrid cell has an output of up to 16.1%. In particular, the fill factor of this solar cell rose significantly by 78.3 %, compared to the fill factor of traditional electrodes (61.4 %), because the metal/contact resistance of the $1\mu\text{m}$ -thick Ag electrode was dramatically reduced [47].

Shin and co-workers [48] developed a multilayer TCE/PEDOT: PSS/Si nanowires/n-Si/ TiO_x hybrid solar cells (HSCs) to resolve problems (deficiencies) of HSCs for practical applications. Highest power conversion efficiency (PCE)10.14% was achieved without TiO_x at layer number 2 (Figure 12) [48]. Remarkable inhibition of the carrier recombination enhancing PCE to 12.10% because of the Si-O-Ti chemical bond formed by deposited TiO_x layer on the backside of the Si. PCE also enhanced by enhancing

Jsc due to the use of silicon nanowire. Resulting PCE is mainly due to the enhancing Jsc and inhibition of recombination [48].

Figure 11 PEDOT:PSS/Si hybrid cells (a) conventional (b) metal electrodes. (c) Curves (d) efficiency distributions. (adapted from reference [47], 2017. permission ACS).

Figure 12 (a,b) Schematic and energy band diagram of a typical MLG/PEDOT: PSS/Si NWs/n-Si/InGa HSC. (Reprinted with permission from reference [48], 2018, Copyright ACS).

2.3 Dye sensitized solar cells

Dye-sensitized solar cells (DSSC) play the leading role in photovoltaic system research with advantages such as the requirement of largely plentiful earth materials, respectable efficiencies, low demand for high-temperature material processing and cell assembly simplicity. The electricity generation process and cell assembly procedures have therefore, been tested well in a typical DSC. They have extremely economical applications.

Brown et al. [49] have identified a successful strategy for combining metallic nanoparticles with a strong resonance of surface plasmon in solar cells sensed by the dye that exceeds four major numbers of metal insertion in most solar cells: recombination within the metal, thermal stability during processing, chemical stability and control of metallic nanoparticles, that separates the chromosomes from the dye to discourage non-radioactive cooling. According to the authors, this new plasmonic photoelectric system led to better absorption of light and the generation of light current in solar cells that are dyed-sensed in nature [49].

Wang et al. [50] fabricated etching patterned (230nm of etching depth) at nano level on commercial fluorine-doped tin oxide (FTO) by nanoimprint lithography and reactive ion etching (RIE) to obtained nanopillar and nanoline arrays which increase FTO resistance (Figure 13) [50]. Authors observed enhanced light scattering from nano-patterned FTO in the wavelength ranges from 400–650nm and improved power conversion efficiency about 2–5% of DSSCs, due to light scattering resulted across the interface with 4 μ m TiO₂ layer in the same wavelength range[50].

Triangular silver nanoprisms were used by Gangishetty and co-workers [51] for light harvesting efficiency (LHE) in a DSSC (Figure 14) [51]. Authors concluded that overall PCE ($32 \pm 17\%$) of the device improved by loading of 0.05% Ag@SiO₂ in the titania photoanode. Such variations were further enhanced at the advance wavelength in LHE according to the authors and further increased Ag@SiO₂ loading, which would have a detrimental effect on the performance of electron collection [51].

Figure 13 (a) FTO patterning procedure using NIL and RIE. (b) Schematic illustration of mechanism of the cell (Reprinted with permission from reference [50] 2012 Copyright ACS).

Figure 14 (a) Schematic illustration of fabrication of the cell (b) Current–voltage ($J-V$) characteristics of the highest performing DSSC. (Reprinted with permission from reference [51] 2013, Copyright ACS).

Kelkar et al. [52] utilized chemically modified egg protein albumen in the quasi-solid state DSSC through appropriate molecular engineering of cross-linking property (Figure 15) [52]. Authors claimed a significantly higher 5.75% efficiency of functionalized egg albumen based gel DSSC than a non-functionalized DSSC having 4.6% efficiency [52].

*Figure 15 Schematic showing denaturation and cross-linking of egg albumen.
 (Adapted from reference [52], 2014, Copyright ACS).*

Karam and co-workers [53] used urchins-like ZnO nanowires (NWs) in the DSSC as photo-anode, in the form of multi-layer, with TiO₂ nanostructures, and core-shell nanostructures have been sensitized to the Ru dye (N719) solution. The photon absorption improves with the number of layers, according to the scientists, but the photovoltaic capacity declines as a consequence of the recombination of the charge. The monolayer of urchins thus demonstrated the maximum efficiency; this can probably be due to the low electric connection between urchin layers. The low conductivity of these nanostructures in the core-shell is emphasized. The authors opined that further optimization can improve the overall efficiency of photoconversion. Similarly Kang et al. [54] prepared mesoscopic nickel(II) oxide (NiO) films and employed them as photocathodes in p-type DSCs. Authors observed good results than others and claimed that this is the first anodic NiO film synthesized with mesoscopic architecture [53].

Figure 16 Schematic illustration of fabrication and mechanism of the cell. (Reprinted with permission from reference [53], 2018, Copyright ACS).

Figure 17 HOMO and LUMO of the dyes. (Reprinted with permission from reference [55], 2019, Copyright (2019) Elsevier)

Computational study of AL-Temime and Alkhayatt [55] has reported series of dye derivative from the ethyl red dye have been studied. The proposed dyes show applicable energy, photoelectric and spectroscopic feature, since new dyes' lowest unoccupied molecular orbital (LUMO) levels are much higher than TiO_2 conduction band (CB), whereas the highest occupied molecular orbital (HOMO) energy levels are lower than the Γ/I_3^- systems redox potential (Figure 17) [55]. This means that the recharge of the colour after the photo-oxidation reaction and the ease of transmitting the electron from the donor to the receiver is easy and that regeneration is possible after this. The investigators found that the dyes investigated were beneficial for the development of new

materials for organic solar cells, with greater photoelectrical strength and a strong photovoltaic output[55].

2.4 Tandem solar cells

Perovskite-based tandem solar cells draw attention to their performance capacity. Liu et al. [56] achieved a maximum efficiency of 16.0% perovskite/polymer solar cell (ITO/PEDOT:PSS/Perovskite/PC₆₁BM/C₆₀-SB/Ag/MoO₃/PolymerBHJ/C₆₀-N/Ag) (Figure 18) [56] is 75% higher than that of the corresponding ~90 nm thick perovskite single-junction device and 65% higher than that of the polymer single junction device. Authors achieved a very high V_{OC} of 1.80 V and a high FF of 77% [56].

Figure 18 (a) Fullerene interlayer materials (C₆₀-N, C₆₀-SB). (b) False color cross-sectional SEM image. (Adapted from reference [56] 2016, Copyright ACS).

Kranz et al. [57] produced a close infrared transparent perovskite with a wavelength of 800 to 1000 nm. The authors stated that a tandem unit with 19.5 % efficiency is feasible, owing to the combination of the near-infrared transparent perovskite top with the CIGS (Cu(In, Ga)Se₂), bottom layer (Figure 19) [57]. There are suggestions and possibilities for systems with capability approaching 27 % of the future development of perovskite/CIGS tandem systems [57].

Figure 19 Schematic of a stacked 4-terminal perovskite/CIGS tandem solar cell. The top cell is a perovskite cell in superstrate configuration and the bottom cell is a CIGS cell in substrate configuration. (Reprinted with permission from reference [57], 2015, Copyright ACS)

Guchhait et al. [58] demonstrated 16 % efficiency of the semi-transparent perovskite solar cell, plus visible light range transparency by 12%, and the near-infrared region transparency by more than 50%. The authors used an optimized perovskite cell for a 4 T (4-terminal) tandem perovskite / Cu-In-Ga-Se₂(CIGS) solar cell (Figure 20) [58] with efficiency (un-certified) of 20.7%, as against a single CIGS cell with an absolute efficiency improvement of more than 7 % [58].

Figure 20 Tandem schematic and $J-V$ curve, of a 4-terminal tandem perovskite/CIGS combination. (Adapted from reference [58], 2017, Copyright ACS).

Introduction of the nano-pyramid structure between the top and the bottom cells, Li and coworkers [59] proposed ultrathin a-Si/c-Si tandem solar cells with an effective light trapping design. According to the authors, significant improvement in the current density of short circuits for the top (48%) and bottom (35%) was observed as a result of superior cell light collection. Of ultrathin tandem cells with a minimum of 8 μm of silicon, transfer efficiencies of up to 13.3 %, this is 29 % better than for a planar cell [59].

Figure 21 (a) Four tandem cell structures: planar; (b) absorption spectra for the cells; (c) photocurrent density for different cells. (Reprinted with permission from reference [59], 2014, Copyright (2014) American Chemical Society)

The output of a hydride vapor phase epitaxy (HVPE)-grown GaAs top cell embedded in a 4-terminal GaAs/Si tandem system, with an efficiency of 29 %, was evaluated by Vasant [60]. By comparing the results with the tandem cell of metalorganic vapor phase epitaxy (MOVPE)-grown GaAs/Si, the authors improved the HVPE-grown GaAs model and give a short-term utility with low-cost III-V deposition techniques for the 31.4 % range [60].

Figure 22 Schematic cross-section of a 4T GaAs//Si tandem device with Al-free GaAs top cell. (Reprinted with permission from reference[60], 2019, Copyright (2019) American Chemical Society)

Conclusion

The researchers attempt to utilize the full range of sunlight for conversion into electricity. The use of multilayer of dyes increases the broad solar spectrum absorption on one hand, however, an increase of layer thickness significantly restricts the solar cell performance. For large-scale development, improvement in the output of hybrid cells is a must. Efficiency can be improved by optimizing several variables. The reduction of the bandgap in order to absorb infrared photons that contain a considerable fraction of the solar spectrum energy must be explored. 70% quantum efficiency for the blue photons has been demonstrated by organic photovoltaic.

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