REVIEW

Polymer-nanocarbon composites: a promising strategy for enhanced performance of organic solar cells

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Abstract

The exigency for sustainable and clean energy resources has led to profound research in development of various generations of solar cells, aiming to control the over-exploitation of fossil fuels and subsequently limit environmental degradation. Among the fast-emerging third-generation solar cells, polymer solar cell technology has gained much consideration due to its potential for achieving economically feasible, lightweight, flexible solar energy harvesting devices. As a predominant research area, at present, the major concerns regarding polymer solar cells include improving conversion efficiency, enhancing absorption bandgap in polymers, limiting photochemical degradation, and remediating low dielectric constant. Nanocarbon materials can be effectively blended with polymers and have been widely reported to enhance the performance of polymer solar cells owing to their desirable characteristics like high electrical conductivity, mechanical strength, thermal stability, non-toxicity, large specific surface area, flexibility, and optical transparency. In this review, we briefly discuss various conjugated polymer-nanocarbon composites, including polymer/graphene derivatives, polymer/graphene quantum dots (GQD), and polymer/carbon nanotubes (CNTs), elucidating their roles in the performance enhancement of polymer solar cells (PSCs).

Keywords Polymer solar cells · Conducting/conjugated polymers · Nanocarbon materials · Conjugated polymer-nanocarbon composites

1 Introduction

The increasing demand for energy all over the world and the environmental pollution caused by excessive usage of conventional fuels necessitates the requirement for eco-friendly energy alternatives. Gearing up to deal with these issues involves a quest for sustainable energy sources along with their efficient harnessing and storage techniques [1, 2]. Among the most sought-after resources, solar energy is a promising, reliable, secure, and renewable energy outlet, provided we are equipped with coherent harvesting and

storage devices. According to the International Energy Agency (IEA), the demand for solar power generation has increased many-fold in the past decade, owing to feasible, environment-friendly, and cost-effective energy production [3].

Progress in technology and science over the years has shouldered the growth of solar cell advancement, presently reaching the third generation of photovoltaics, which are smoothly making way for the upcoming fourth generation [4]. A comparative study of the different generations of photovoltaics is given in Table 1.

The first-generation, silicon-based solar cells, comprising single-crystalline and polycrystalline cells, are technologically mature and are widely commercialized [11, 12]. However, high cost and complex manufacturing demands for first-generation photovoltaics paved the way for second-generation solar cells based on thin-film technology involving materials like amorphous silicon, cadmium-telluride (CdTe) [11, 12], copper indium gallium di-selenide (CIGS) [11–13], copper indium di-selenide (CuInSe$_2$) [14], and copper-zinc-tin-sulfide (CZTS) [8, 15, 16].

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Table 1 A comparative study of the different generations of photovoltaics, and their types and characteristics. The maximum reported efficiencies are taken from the NREL database

SOLAR CELL GENERATIONS			
GENERATIONS	TYPES (Maximum reported PCE in bracket)	ADVANTAGES	DISADVANTAGES
First	Silicon-based: Single crystalline (27.6%) Polycrystalline (23.3%)	• Efficiency up to 25% [5]	• Difficult manufacturing process • High cost • High energy consumption [6]
Second	Thin-film solar cells (GaAs thin film crystal, 29.1%)	• Cost-effective [7] • Better effective material utilization	• Less availability of materials like gallium and indium • Toxicity of materials used [8]
Third	Organic photovoltaic cells (OPV) (19.2%) Perovskite solar cells (26%) Dye-sensitized solar cells (DSSC) (13%) Quantum dot solar cells (18.1%)	• Lightweight • Low cost • Flexibility	• Low conversion efficiency (perovskite solar cell can be considered an exception) • Device stability [9, 10] • Immature technology

Thin-film solar cells are cost-effective as they ensure effective material utilization compared to silicon solar cells [7]. The main bottleneck faced by thin-film solar cells is the scarcity of raw materials, which are often toxic [7, 8].

Figure 1 depicts the highest confirmed laboratory photoconversion efficiency for various photovoltaic cells from 1975 to 2023. Here, emerging photovoltaics have shown a tremendous increase in conversion efficiency from the 1980s, with the least recorded efficiency reaching 13% (inorganic cells and dye-sensitized cells) and the highest recorded efficiency at 33.7% (perovskite/Si tandem monolithic) by 2023 [17].

Presently, the new generation of solar cells—the third-generation photovoltaics based on nanocrystals, polymers, dyes, perovskites, and organic materials—is a highly flourishing field in solar energy research [18]. Even though the achieved power conversion efficiency and stability are low in most cases, third-generation solar cells are renowned due to their numerous practical applications [10]. Third-generation solar cells have been much superior over the past two generations in terms of environmental impact, material abundance, low-cost manufacturing techniques, flexibility, and lightweight [19, 20]. The performances of organic solar cells (attained a PCE of 18.2%) and various quantum dot cells (achieved an efficiency of 18.1%) with a low cost/watt balance are highly notable. In view of their advantages like potential wide-scale production and quick energy payback times, organic solar cells have received a lot of attention over the past two decades, indicating a promising future for commercialization and for meeting the terawatt energy challenge. This, further points towards the fact that composites of organic polymer materials have the possible potential to improve photoconversion efficiency, keeping expenses under control, and such photovoltaics have been tremendously explored recently [21].

Organic photovoltaics are flexible and lightweight compared to rigid crystalline silicon solar cells. These properties, along with the factor of being low cost, become significant in applications like the Internet of Things (IoT) [22] and remote area power distribution, where long-term usage of batteries has become impracticable. Even though thin-film solar cells also have the inherent advantage of flexibility, the requirement of easily bendable substrate metal foil that withstands high fabrication temperatures (CIGS (> 550 °C) and CdTe (> 600 °C)) increases the complexity of cost and technology [23]. Hence, organic photovoltaics have become significant despite their limitations, like immature technology and lack of long-term operational stability. Table 2 summarizes the mechanical hardness of different types of solar cells.

While conventional thin-film solar cells bend at a curvature radius of a few millimeters, organic cells outperform them in terms of flexibility. Kaltenbrunner et al. [26] have reported that glueing the flexible device to a pre-stretched elastomer allows the devices to resist quasi-linear compression to below 70% of their original area. Additionally, they discovered that the device performance suffered only minimal loss after 20 complete cycles of cyclic compression and stretching to 50% without any discernible damages on the peripheral contact points of the device. The extraordinary flexibility and specific weight of organic photovoltaics make them an ideal ultrathin-film power source for Internet of Things applications [28]. Replacing indium-tin-oxide (ITO) electrodes with flexible transparent conductive electrodes like conductive polymers or conductive carbon nanomaterials or their hybrid composites will result in an increment in the pliability of these solar cells.

Another emerging technology, using conjugated polymers as donor materials in solar cells, has also been reported to enhance the device performance. According to reported studies, employing a low bandgap polymer as a donor and fullerene derivative as an acceptor effectively pushes efficiency
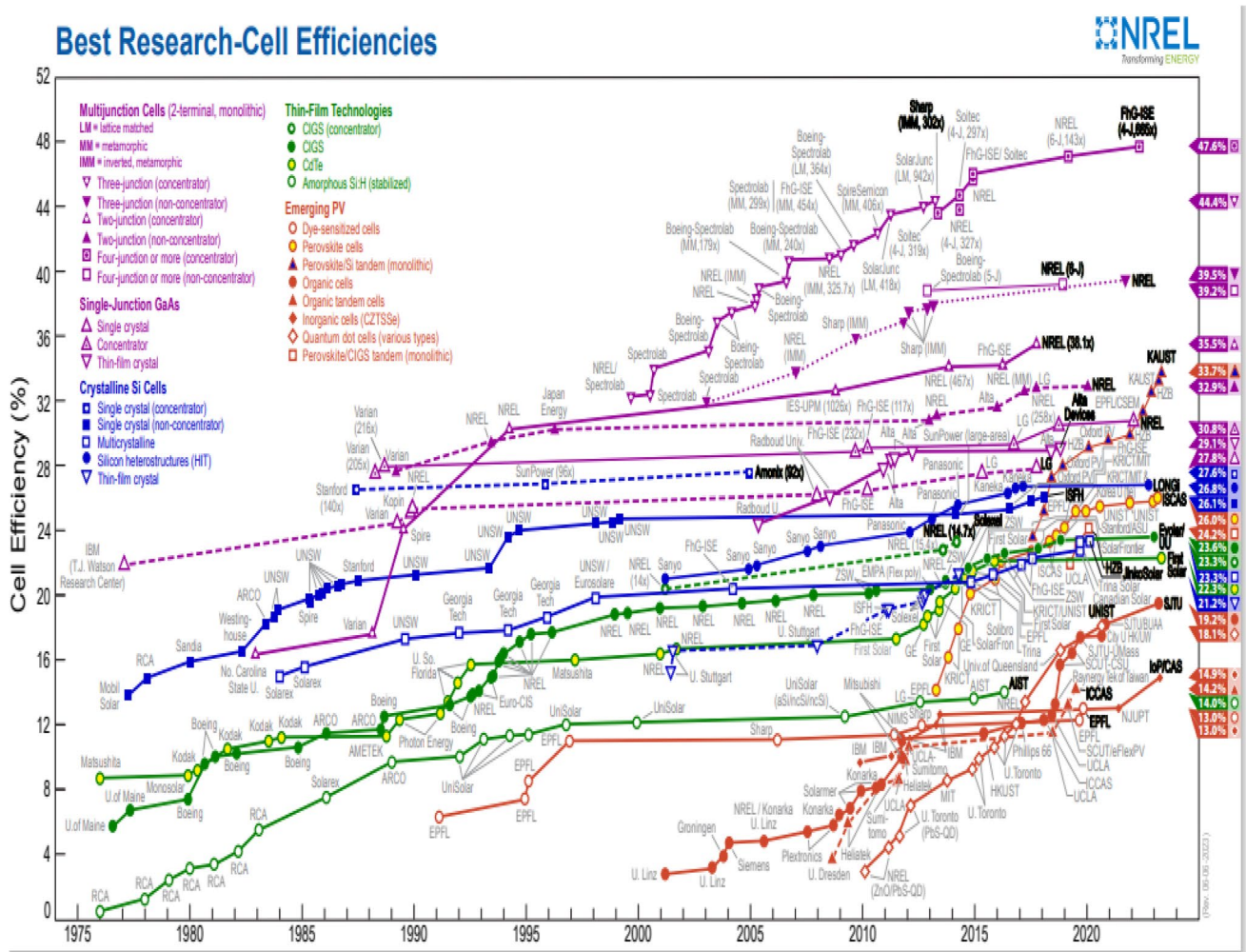
Fig. 1 Recorded efficiencies of all generations of solar cells (1975 to 2023) (Source: NREL efficiency report) [17]

Table 2 Mechanical hardness of various types of solar cells

Materials	Substrate	Curvature radius	Reference
CdTe (3–4 μm)	PI–7.5 μm	Few mm	[24]
Cu(In,Ga)Se2 (2 μm)	PI–25 μm	20 mm	[25]
a-Si:H/μc-Si:H (3 μm)	0 μm	3.5 mm	[24]
GaAs (~ 5 μm)	PET–50 μm	< 5 mm	[24]
Organic PV (200 nm)	PET–1.4 μm	Stretchable	[26]
Perovskite (250–300 nm)	PET–1.4 μm	Stretchable	[27]

beyond 10%. Adaptable and tunable physical and chemical properties [29] of polymers, including electrical conductivity, have been used in various applications [30–32]. Owing to their three-dimensional network structure, polymer templates can be employed to create mesoporous materials or polymeric matrices in solid electrolytes [33–35]. In addition, certain polymers have strong carrier mobility, which makes

it possible for them to serve as electron and hole transfer materials. Many functional groups in polymers aid in controlling the bulk morphology and interfacial layers to passivate defects, enhancing the performance of devices [36, 37]. Polymers can also be employed as photoactive layers or buffer layers in organic photovoltaics owing to their varied structures and modified functional groups, which tune the optical absorption and electron mobility [38, 39]. Easy processing methods of polymers make the fabrication of organic solar cells more viable and cost-effective.

1.1 Device structure and working of polymer solar cells

Polymer solar cells work based on photoexcitation, leading to exciton generation followed by charge separation by proper energy level alignment of different layers (Fig. 2a). Well-defined energy level arrangement of different layers in the photovoltaic device, as shown in Fig. 2b, enables a highly
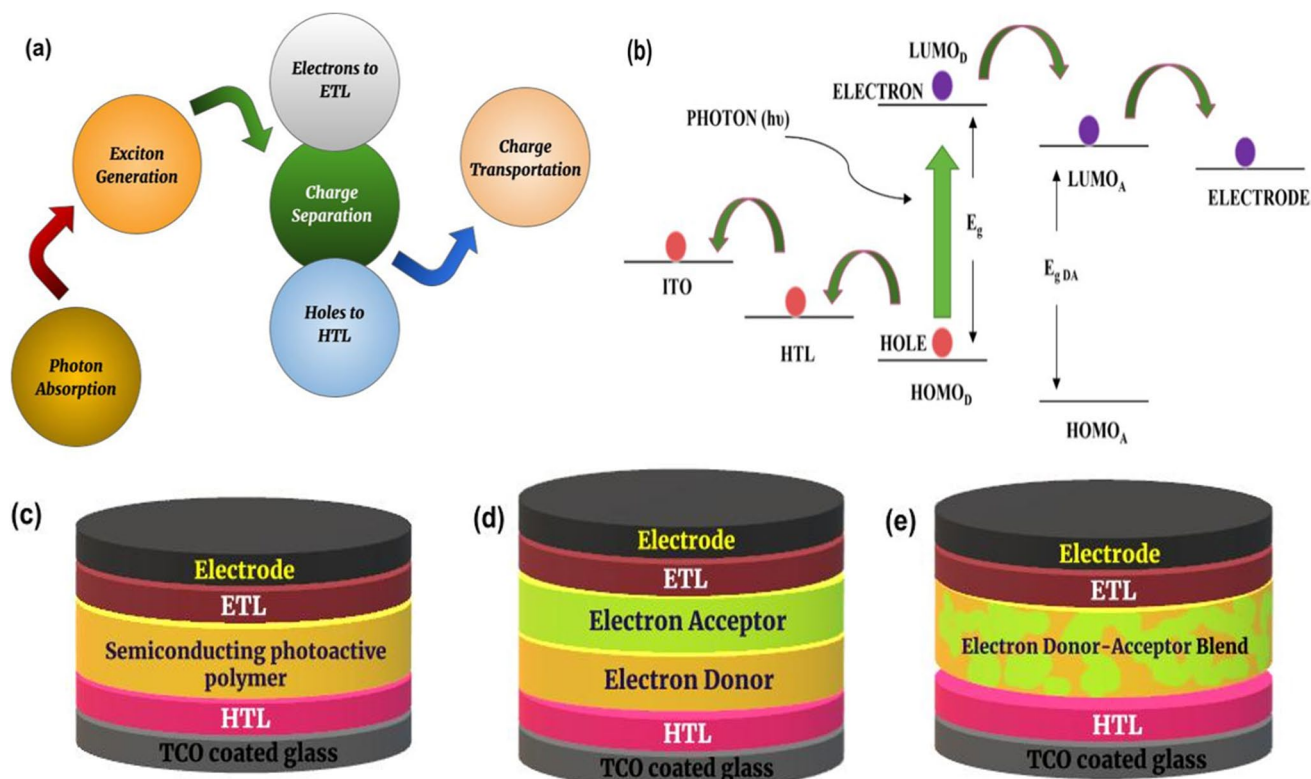
Fig. 2 Schematic representation of **a** working processes and **b** energy level alignment of a polymer solar cell. Structural arrangement of **c** single layer, **d** bilayer, and **e** bulk heterojunction polymer solar cells

directional flow of charges and efficient charge separation. The electrons from the donor polymer are excited to the LUMO$_D$ (Lower Unoccupied Molecular Orbit) levels upon light irradiation, forming excitons. At the donor–acceptor interface, the electrons from the generated excitons are transferred to the LUMO level of electron acceptor (LUMO$_A$) and then to the electrode. Likewise, the generated holes move from the Highest Occupied Molecular Orbit of the Donor material (HOMO$_D$) to the other electrode through intermediate layers like hole transport layer (HTL). The generated photocurrent and the cell parameters like photoconversion efficiency (PCE), fill factor (FF), short circuit current (J_{SC}), and open circuit voltage (V_{OC}) depend on a number of factors like incident light intensity, carrier diffusion length, and surface recombinations [40–44].

The structure of polymer solar cells varies depending on the materials and combinations used; these can basically be classified into three types. A single-layer polymer photovoltaic (Fig. 2c) comprises a photoactive layer sandwiched in between the charge transport layers, which are followed by the electrodes. In case of a bilayer polymer solar cell, the photoactive layer comprises an electron donor and an acceptor material stacked one above the other, as shown in Fig. 2d, whereas, in a bulk heterojunction, a donor–acceptor blend, as given in Fig. 2e, is used as the active layer.

Apart from these structures, many reported studies have included additional layers or have excluded a few layers to enhance the operational efficiency and viability of the fabricated device [45–52]. We shall be coming across several such device structures and the roles of materials used in the upcoming sections.

2 Polymer-nanocarbon composites—significance

Each layer in a polymer photovoltaic plays a significant role in the device functioning, and thereby the selection of materials for each layer is crucial in enhancing the performance. Even though conducting polymers have many advantages over conventional materials, issues like low hole mobility, narrow light absorption range, lower efficiency, and stability call for further exploration to overcome the limitations. As an effective technique of remediation, the conducting polymers can be blended with various nanocarbon materials. The high surface-to-volume ratio of nanocarbon materials helps in tuning properties like absorption range, whereas the size of these materials aids in the miniaturization of devices [53]. The other noteworthy properties of carbon nanomaterials include high conductivity, mechanical strength, and

good interaction with external agents. Hence, the blending of polymers and carbon nanomaterials will complement each other to make a positive impact on the device structure and performance [54–57]. Table 3 gives a brief outlook on the advantages and disadvantages of polymer-nanocarbon composites.

3 Polymer-nanocarbon composites— synthesis

Preparation of polymer-nanocarbon composites often involves less complex, and comparatively scalable techniques, which can either be making a composite out of separately synthesized polymer and nanocarbon or be co-synthesis for obtaining the composite. Zhang et al. [58] have discussed special strategies like homogeneous, laminate, alignment, and network architectures to enhance the desired properties of polymer-nanocarbon composites. To attain the homogeneous architecture of nanocarbon in a polymer matrix, different methods like powder-blending [59], melt blending [60], solution blending [61], and in situ polymerization [62] can be employed. Methods like evaporation [63], vacuum filtration [64], scaffold infiltration [65], and layer-by-layer assembly [66] can be used to obtain the laminate architecture of nanocarbon in a polymer matrix. Aligning nanocarbon, especially one-dimensional materials like CNTs, in a particular direction on a polymer matrix can be done by methods like array infiltration [67] or by applying shear force [68], electric field [69], or magnetic field [70].

Qi et al. [71] have reported the enhancement of electrical conductivity in polystyrene (PS) nanocomposites upon the addition of graphene, which was selectively localized by the addition of polylactic acid (PLA) (Fig. 3a, b). Chougule et al. [72] reported enhancement in dielectric property of poly(vinylidene fluoride) by hybriding it with different concentrations of nanocarbons (Fig. 3c, d, e).

As seen in the above examples and other reported studies [73], nanocarbon materials can help in enhancing several desired properties, like conductivity and dielectric constant,

in polymers, which would, in turn, make them more compatible as solar cell materials. In this review, we shall discuss the structure and performance of polymer solar cells, focusing on reported studies on nanocarbon-polymer composites at different roles and their impacts on device performance.

4 Polymer-nanocarbon composites in polymer solar cells

The blending of polymers with nanoparticles consequently results in tuning of electronic and optical properties, thereby influencing the performance of polymer photovoltaics. Fullerenes, carbon dots, CNTs, graphene, and other carbon-based nanomaterials have been reported as potential additives in polymers that can enhance photovoltaic performance. In addition to high surface-to-volume ratio and size tunability, these materials exhibit excellent optical, chemical, and physical properties, which provide shorter routes to the light-generated carriers, reducing the chance of undesired recombinations. The properties like good thermal and photostability, high conductivity, tunable interaction with external agents, high mechanical strength, solution-processability, and chemical tunability make it possible for the nanocarbon materials to enhance the performance, flexibility, and durability of the solar cells [74–83].

4.1 Polymer-nanocarbon composites as active layer in polymer solar cells

The active layer plays the most crucial role in the operation of a third-generation solar cell, as it acts as the basic site for photoexcitation. In case of polymer photovoltaics, the nature of active layer can vary depending on the device structure. Single-layer polymer solar cells have an active layer made of materials like polyflourenes, polythiophenes, phthalocyanine, and polypyrenes [84], where the scope of nanocarbon addition is ruled out. It is not because nanocarbon materials cannot enhance the performance there, but rather, on addition of any different material to the active layer, the structure

Table 3 A brief outlook on the advantages and disadvantages of polymer-nanocarbon composites

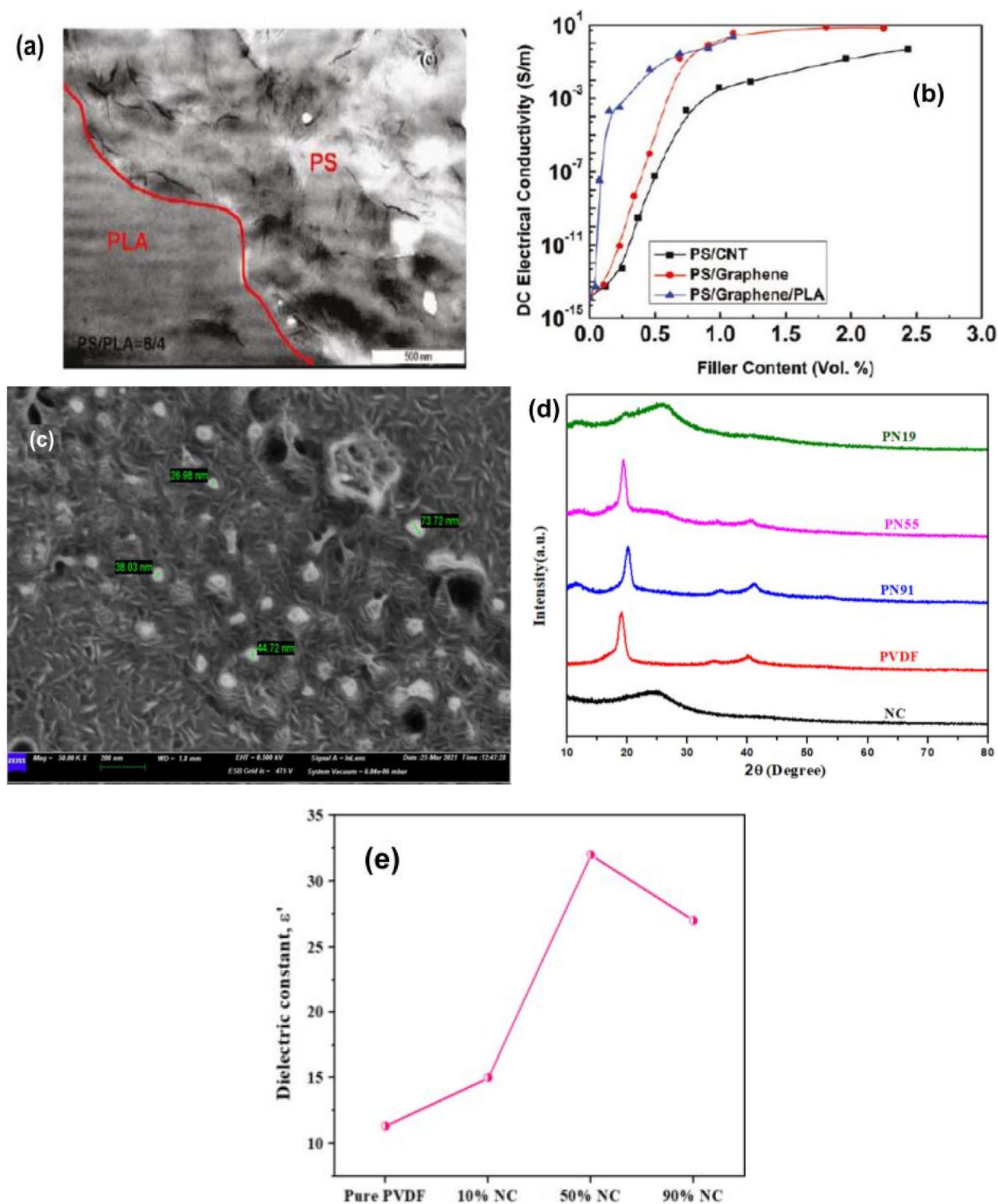| Polymer-nanocarbon composites	
Advantages	Disadvantages
• High tunability of optical and electronic properties by simple compositional engineering • Combines the advantages of both polymers and nanocarbon materials • Nanocarbon materials can enhance the durability of polymer hybrids • Flexibility • Scope for large-scale production • Increases the environmental compatibility • Cost-effectiveness compared to other solar cell materials	• Immature technology • The synthesis of hybrid materials is more sophisticated compared to their non-hybrid counterparts • Difficulty in blending polymers with nanocarbon materials to get optimal optical and electronic properties. Often, when one property is enhanced, another has to be compromised

Fig. 3 **a** SEM image and **b** variation of electrical conductivity with graphene content of PS/graphene/PLA nanocomposite. Reprinted with permission from [71]; **c** SEM image of poly(vinylidene fluo-ride)–nanocarbon composite; **d** XRD spectra and **e** dielectric constant of poly(vinylidene fluoride) with varying nanocarbon content. Reprinted with permission from [72]

can no longer be called a "single layer." When it comes to the case of bilayer structure, the active layer comprises both electron donor and acceptor, where the use of nanocarbon composites has already been reported. The most prominent bulk heterojunction structure accounts for the majority of reported works with polymer-nanocarbon composites for organic photovoltaics.

Ke et al. [85] fabricated a bulk heterojunction device with a combination of silicon-based naphthalocyanines (SiNC) and phthalocyanines (SiNC) embedded in PCBM/P3HT (where PCBM is [12, 12]-phenyl-C_{61}-butyric acid methyl ester and P3HT is poly(3-hexylthiophene)) matrix as the light-harvesting active layer. The panchromatic photovoltaic with fullerene/quaternary polymer active layer showed broad range absorption extending to the IR region. The device showed a maximum PCE of 3.8%, corresponding to V_{OC} of 6.5 V and J_{SC} of 10.8 mA/cm^2, when the weight percentages of SiPC and SiNC were 7.5% and 5%, respectively, whereas the device with ternary polymer/fullerene photosensitive layer with the incorporation of 10% SiNC yielded a PCE of 3.68% and J_{SC} of 9.72 mA/cm^2, V_{OC} being the same as that of its quaternary counterpart. The enhancement of device performance with the addition of SiNC and SiPC is attributed to complex mechanisms like cascade charge transfer, parallel-like charge transfer, and energy transfer kinetics. Raboui et al. [86], for the first time, paired oxy phosphorus tetrabenzotriazacorrole (POTbc) with a C_{70} fullerene electron donor in a planar heterojunction organic solar cell, obtaining a PCE of 1.96%. A notable J_{SC} of 6.39 mA/cm^2 was recorded, owing to the dual absorption of POTbc in the visible region of the spectra.

Using 0D quantum dots (GQDs) obtained from 2D graphene is proven to be a successful strategy for enhancing the efficiency of active layers in organic solar cells. Having lateral dimensions of less than 10 nm and thickness of less than 2 nm, GQDs display quantum confinement and edge effect [87], with the added advantages of being chemically inert and non-toxic. Compared to graphene, GQDs provide a large specific surface area [88] and better surface grafting through π-π conjugate bonding, favoring their usage for light absorption and exciton generation. Li et al. [89] used GQDs (graphene quantum dots) of uniform size ranging from 3 to 5 nm, having green fluorescence as electron acceptors, with the bulk heterojunction device giving a PCE of 1.28%. The energy level alignment, as shown in Fig. 4a, makes charge transfer easier as compared to the structure without GQDs. The GQDs provide greater carrier separation interfaces and charge transfer pathways, enhancing the J_{SC} from 0.078 mA/cm^2 (without GQDs) to 6.33 mA/cm^2. Kim et al. [90] compared the performance of oxidized GQDs (GOQDs) and GQDs reduced to varying extents by varying hydrothermal reduction time

(Fig. 4b) as additives to PTB7/PC71BM (where PTB7 is thieno[3,4b]thiophene-alt-benzodithiophene (PTB7)) active layer in bulk heterojunction device. Photovoltaics incorporated with reduced GQDs hydrothermally reduced for 5 h showed the best performance, yielding a PCE of 7.6% and a fill factor of 67.6%, owing to the attained balance of electrical conductivity and light absorption. Gupta et al. [91] studied the performance of aniline functionalized GQDs and graphene sheets as additives to the P3HT active layer, with varying GQDs and graphene sheets (Fig. 4c). Incorporation of 1% aniline functionalized GQDs to the P3HT active layer showed the best result with a PCE of 1.14% and a fill factor of 53%.

Li et al. [92] incorporated GQDs synthesized from double-walled CNTs into a P3HT-PCBM mix with varying concentrations of PCBM, and the blends were tested as active layers in bulk heterojunction polymer photovoltaics with structure ITO/PEDOT:PSS/P3HT:PCBM:GQDs/LiF/Al. Among different devices tested, the one with an active layer made of 1:0.6 weight ratio of P3HT:PCBM and GQDs blend outperformed other devices with a PCE of 5.24% and J_{SC} of 26.46 mA/cm^2 as shown in Fig. 4d. The enhancement of J_C with an increase in PCBM concentration ratio up to 1:0.6 is attributed to the phase separation, which promotes charge transport and reduces bimolecular carrier recombinations. However, when PCBM concentration is increased beyond this limit, the optical density of the blend film is seen to decrease, causing a drop in J_{SC} value and, thereby, the overall device performance. Using GQDs functionalized with different molecular weights of polyethylene glycol (PEG), Novak et al. [93] (2016) enhanced the performance of P3HT:PCBM active layer, achieving a maximum PCE of 4.14% for 200 PEG-GQD in the P3HT:PCBM blend. An increment in PEG length resulted in decreased device performance for functionalized GQDs, and GQDs functionalized with short chain length PEG (200PEG-GQD) gave the best result. The usage of PEG-functionalized GQDs made exciton dissociation in P3HT faster and enhanced the active layer absorption, as shown in Fig. 4e. To validate the impact of functional groups, GQD concentration was maintained at 0.025 mg/mL, and the addition of pristine GQD did not improve the overall efficiency but rather enhanced the short circuit current from 12 to 13.4 mA/cm^2.

Owing to their unique properties, carbon nanotubes (CNTs) have also been reported as additives in the photoactive layer of polymer solar cells. Single-walled carbon nanotubes (SWCNTs) (at a concentration of 0.5%) were blended into the P3HT:PCBM photoactive layer of bulk heterojunction polymer photovoltaic device by Kymakis et al. [94], and this blending boosted J_{SC} by about 30% and PCE by about 40% without altering the V_{OC}. The incorporation of SWCNTs made charge transfer, enhancing the J_{SC} from 3.75 to 4.95 mA/cm^2. Bhatia et al. [95] functionalized
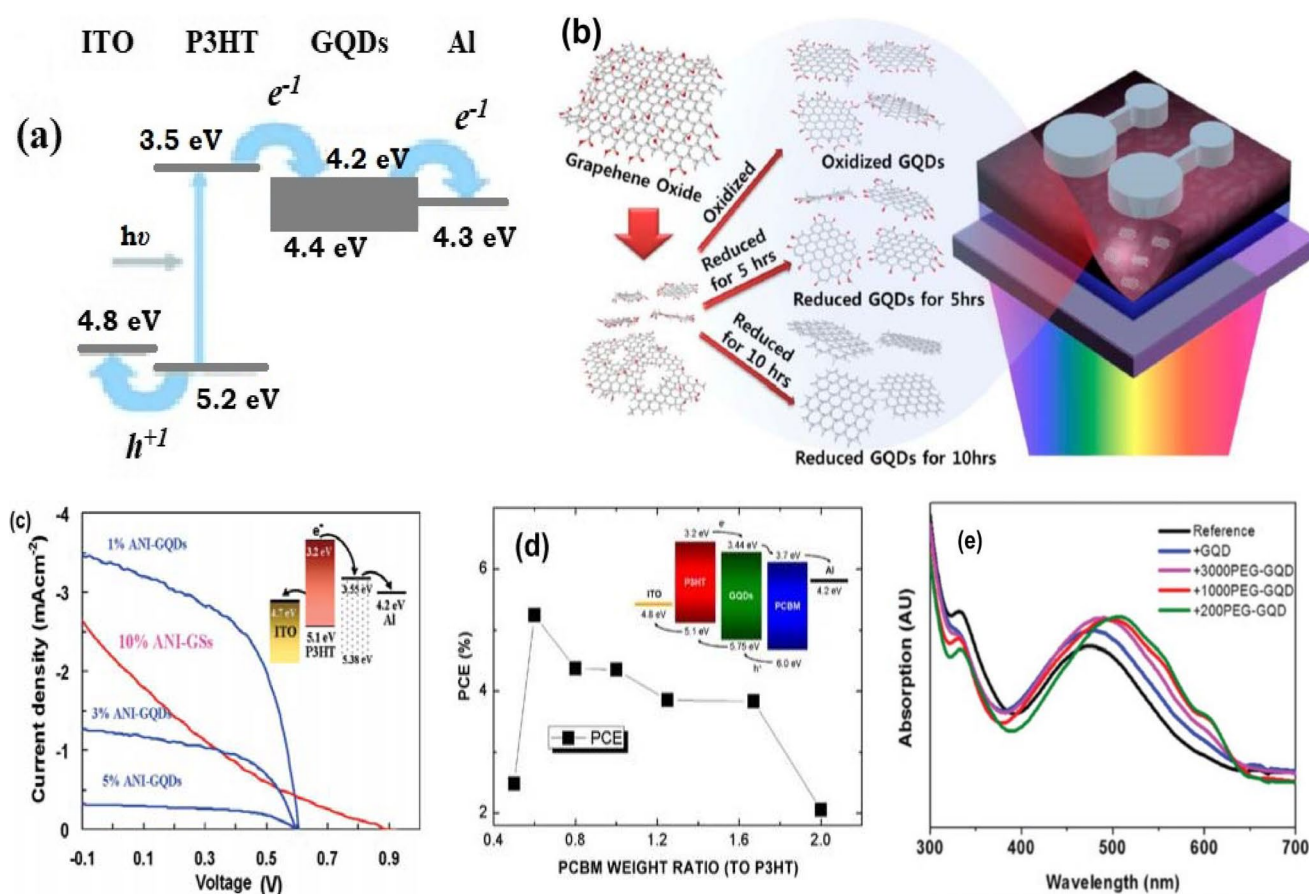
Fig. 4 a Energy level alignment of ITO/PEDOT:PSS/P3HT:GQDs/Al device structure. Reprinted with permission from [89]. **b** Synthesis route of oxidized GQDs (GOQDs) and GQDs reduced to varying extends by varying hydrothermal reduction time as additives to PTB7/PC71BM active layer in bulk heterojunction device. Reprinted with permission from [90]. **c** Comparison between J-V curves of photovoltaics fabricated with aniline functionalized GQDs and graphene sheets as additives to P3HT active layer, with varying GQDs and graphene sheets and (inset) the energy level alignment of differ-ent layers in the solar cell. Reprinted with permission from [91]. **d** Comparison of device performance of ternary photovoltaics with P3HT:PCBM:GQDs blend as the active layer, with varying concentrations of PCBM and (inset) the energy level alignment of different layers in the device. Reprinted with permission from [92]. **e** Comparison between UV–visible absorption spectra of GQDs functionalized with different molecular weights of PEG. Reprinted with permission from [93]

MWCNTs with two different aryl azides, which are nitrene generation precursors, and these functionalized MWCNTs were incorporated into the P3HT:PCBM active layer. The reported performance enhancement is attributed to the shortening of exciton dissociation pathway brought about by the functionalized MWCNTs. In 2021, Khan et al. [96] incorporated varying concentrations of MWC-NTs into the P3HT:PCBM photoactive layer of organic photovoltaics with device structure ITO/PEDOT:PSS/P3HT:PCBM:MWCNTs/Ca/Al. The device with a 4% concentration of MWCNTs in the active layer gave the best performance with a PCE of 1.88%.

2D nanocarbon materials like graphene (G) and its derivatives have also been reported as additives to the polymer-based active layer materials of organic solar cells. Liu and colleagues [97] fabricated a polymer solar cell with solution-processable functionalized graphene (SPF-G) as an electron acceptor additive to the P3OT (poly(3-octyltheophene)) donor in a bulk heterojunction structure, achieving an efficiency of 1.4% for SPF-graphene concentration of 5 wt%. Later, the same group [54] replaced P3OT with P3HT, attaining a PCE of 1.1% with the incorporation of 10% weight of SPF-graphene. In another reported study by Wang et al. [98], with a similar device structure and an active layer comprising SPF-graphene, P3OT, and PCBM composite, a PCE of 1.14% was achieved.

All the above-analyzed literature elucidates the effectiveness of nanocarbon materials as additives to polymers in the photoactive layer of polymer solar cells. Table 4 gives a comparison between different device structures, materials, and solar cell parameters of different reported organic photovoltaics with nanocarbon-polymer composites as active

Table 4 Comparison between different device structures, materials, and solar cell parameters of different reported organic photovoltaics with nanocarbon-polymer composites as active layers

Device structure	Active layer hybrid material	PCE (%)	FF (%)	J_{SC} (mA/cm^2)	V_{OC} (V)	Ref
ITO/ZnO/P3HT:SiNC-1:PCBM/MoO$_x$/Ag	P3HT:SiNC-1:PCBM	3.68	58.3	9.72	0.65	[85]
ITO/ZnO/P3HT:SiPC-0:SiNC-1:PCBM/MoO$_x$/Ag	P3HT:SiPC-0:SiNC-1:PCBM	3.89	55.4	10.80	0.65	[85]
ITO/PEDOT:PSS/C$_{70}$ fullerene/POTbc/BCP/Ag	C$_{70}$ fullerene (electron donor)/POTbc	1.96	48.0	6.39	0.64	[86]
ITO/PEDOT:PSS/P3HT:GQDs/Al	P3HT:GQDs	1.28	30.0	6.33	0.67	[89]
ITO/PEDOT:PSS/PTB7/PC$_{71}$BM:GQDs/TiO$_x$/Al	PTB7/PC$_{71}$BM:GQDs	7.60	67.6	15.20	0.74	[90]
ITO/PEDOT:PSS/P3HT:ANI-GQDs/LiF/Al	P3HT:ANI-GQDs	1.14	53.0	3.51	0.61	[91]
ITO/PEDOT:PSS/P3HT:PCBM:GQDs/LiF/Al	P3HT:PCBM:GQDs	5.24	33.0	26.46	0.60	[92]
ITO/PEDOT:PSS/P3HT:PCBM:200PEG-GQDs/Al	P3HT:PCBM:200PEG-GQDs	4.10	54.2	13.80	0.55	[93]
ITO/PEDOT:PSS/P3HT:PCBM–SWNTs/Al	P3HT:PCBM–SWNTs	1.40	52.0	4.95	0.55	[94]
ITO/PEDOT:PSS/P3HT:PCBM–functionalized SWNTs/Al	P3HT:PCBM–functionalized SWNTs	2.00	42.0	9.18	0.49	[95]
ITO/PEDOT:PSS/P3HT:PCBM:MWCNTs(4%)/Ca/Al	P3HT:PCBM:MWCNTs (4%)	1.88	44.0	8.64	0.49	[96]
ITO/PEDOT:PSS/P3OT:SPF-graphene (5%)/LIF/Al	P3OT:SPF-graphene (5%)	1.40	37.0	4.20	0.92	[97]
ITO/PEDOT:PSS/P3HT:SPF-graphene (10%)/LIF/Al	P3HT:SPF-graphene (10%)	1.10	38.0	4.00	0.72	[54]
ITO/PEDOT:PSS/P3OT:PCBM–SPF-graphene (9%)/LiF/Al	P3OT:PCBM–SPF-graphene (9%)	1.14	37.0	4.60	0.67	[98]

layers. The reported polymer-nanocarbon blends have shown improved conductive properties, microstructure, temperature stability, and visible light absorption compared to the bare polymer materials. Most of the studies have shown that incorporation of nanocarbon materials has improved the fill factor and short circuit current, thereby increasing the light-conversion efficiency, owing to better charge separation and faster charge transportation.

4.2 Polymer-nanocarbon composites as charge transport layers in polymer solar cells

Effective separation of excitons generated by the photovoltaic effect in the active layer, followed by the transportation of charges to desired directions with a minimal number of undesired recombinations, makes up a crucial and complicated process in the operation of an organic solar cell. The charge transport layers, be it HTL (hole transport layer) or ETL (hole transport layer), play important roles in the extraction of charges from the active layer and their movement in specific directions.

Even though there are reported works based on materials like WS$_2$ [99] and metal oxides [100], the majority of efficient materials reported for HTL application in organic solar cells fall under the category of polymers, like the well-known PEDOT:PSS [101, 102], and their composites [103–105]. Moon et al. [106] used nitrogen-doped GQDs (n-GQDs) along with PEDOT:PSS as the HTL in PTB7:PC$_{71}$BM-based organic solar cells to enhance the energy downshift and, thereby, hole extraction. Nitrogen-doped GQDs, whose optical characteristics can be tuned by varying treatment temperatures, were synthesized by solvothermal cutting of poly-acrylonitrile carbon frameworks. As a result of GQD incorporation, there was a notable increase of PCE up to 14.5%. Dang et al. [107] functionalized multiwalled carbon nanotubes (MWCNTs) using boronic acid and blended them with PEDOT:PSS to form the HTL of PCDTBT:PC71BM-based organic solar cells. A 28% hike in PCE is reported upon the addition of 0.4% weight of br-MWCNTs which is attributed to the increase in short-circuit current caused by enhanced conductivity and hole mobility. Zhang et al. [108] hybridized unzipped single-walled carbon nanotubes (u-SWCNTs) with PEDOT:PSS, forming the HTL in PBDB-T-2F:IT-4F-based polymer solar cells, which yielded a PCE of 14.6%. The notable enhancement in fill factor and short circuit current is ascribed to the improved conductivity and carrier mobility induced in the PEDOT:PSS as a consequence of u-SWCNT incorporation.

Among the reported nanocarbon materials used as additives in polymer HTLs, graphene and its derivatives take up a major share, owing to the exceptional properties of these two-dimensional nanomaterials. Dericiler et al. [109] used electrochemically exfoliated graphene, synthesized using sulfate salts, to modify the PEDOT:PSS HTL of organic photovoltaics based on P3HT:PCBM active layer. The addition of graphene enhanced the PCE by about 66%, which indicates improved carrier transportation efficiency of the HTL. Maity et al. [110] used an interlayer of HNO$_3$-treated graphene between PEDOT:PSS and ITO layers in PTB:PC71BM-based organic photovoltaics, yielding an efficiency of 7% with a J_{SC} of 14.3 mA/cm^2. When this same formation was used, excluding the ITO layer, the device performance improved even higher, reaching a PCE of 8.4%, with a J_{SC} of 16.1 mA/cm^2, keeping the V_{OC}

constant at 0.75 V. Similarly, Hilal et al. [111] have also reported incorporating graphene additives to PEDOT:PSS to form the anode interfacial layer, where the chemical interactions between graphene and PEDOT:PSS enabled increased electron transfer from graphene to PEDOT:PSS, increasing the conductivity of graphene by giving it a net positive charge, consequently resulting in an enhanced PCE of 4.52%. Iakobson et al. [112] studied the performance of polyaniline-PAMPSA (poly(2-acrylamido-2-methyl-1-propane sulfonic acid)-graphene nanosheet composites as an HTL material in P3HT:PC$_{70}$BM-based organic solar cells

by varying the range of graphene oxidization. The unoxidized graphene nanosheets showed better performance owing to their increased roughness, which, in contact with the active layer, promotes better exciton separation and hole extraction. Pei et al. [113] have reported sulfonated graphene (SG)–modified PEDOT:PSS HTLs for PM6:Y6 and PM6:L8BO-based devices, attaining notably high PCEs of 17.48% and 18.56% respectively. The sulfonated graphene, on one hand, reduced the undesired energy barriers and on the other hand improved the surface morphology and conductivity enabling faster hole extraction.
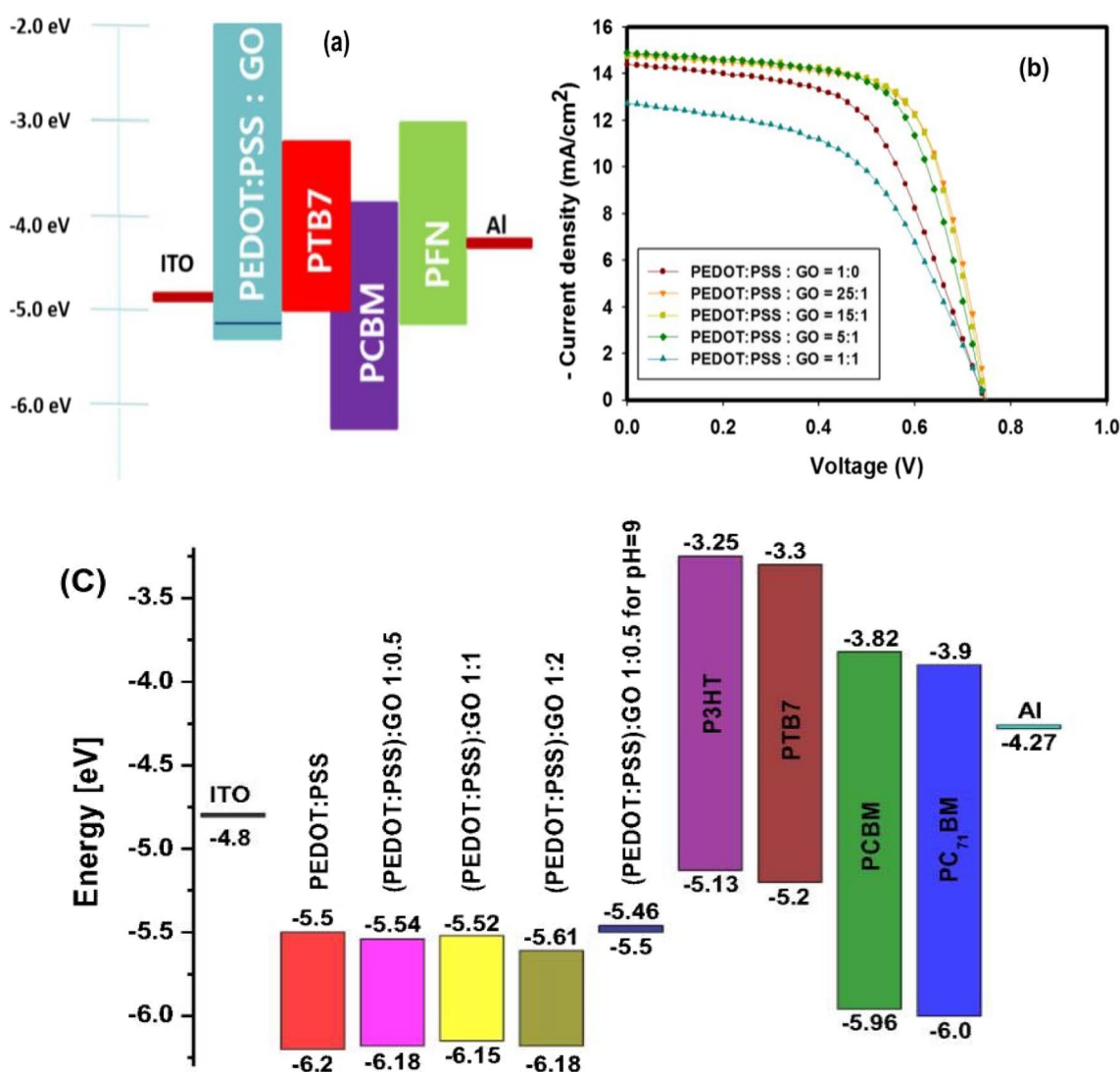

Fig. 5 a Energy level alignment of ITO/PEDOT:PSS:GO/PTB7:PCBM/PFN/Al device structure (PFN is poly[(9,9-bis(3′-(N,N-dimethylamino)propyl)-2,7-fluorine)-alt-27-(9,9-dioctylfluorene)]). **b** Comparison of J-V characteristics for devices fabricated with varying (PEDOT:PSS):GO ratios in the HTL. Reprinted with permission from [118]. **c** Energy level diagrams of the different active layer and charge transport materials, including various ratios of [PEDOT:PSS]:GO composites, used in the study by Iwan et al. Reprinted with permission from [119]. The superior performance of devices with [PEDOT:PSS]/GO double-decked HTL compared to devices with single-material HTLs-PEDOT:PSS and GO separately, in terms of **d** current density. **e** Open-circuit voltage; **f** fill factor; and **g** PCE. Reprinted with permission from [120]
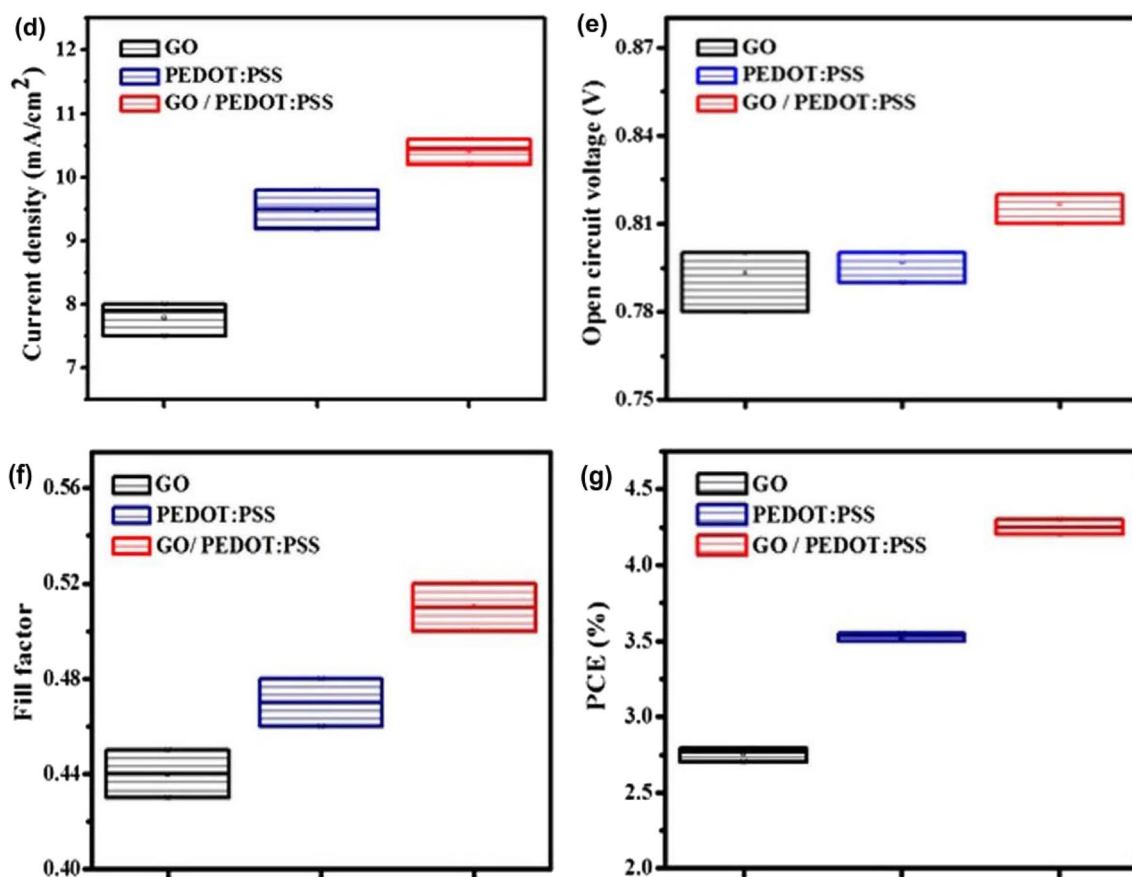
Fig. 5 (continued)

Graphene oxide (GO) [114–116], which is a popular and potential derivative of graphene, is one of the most widely reported nanocarbon materials to be used as an additive to modify the polymer HTL of organic photovoltaics. Ozcan et al. [117] doped PEDOT:PSS with GO to form the HTL of P3HT:$PC_{71}BM$-based inverted organic solar cell, attaining an efficiency of 2.75%, owing to the superior electronic properties brought about by GO doping. Raj et al. [118] have also reported a similar work, blending PEDOT:PSS and GO to form the HTL of PTB7:PCBM-based polymer photovoltaics, yielding a maximum efficiency of 7.68%. The energy level alignment, as shown in Fig. 5a, facilitates the desired directional flow of electrons and holes. The HTL incorporated with GO shows good conductivity, enabling efficient hole extraction and transfer, thereby improving the performance parameters of the device. Figure 5b shows the J-V characteristics for devices fabricated with varying (PEDOT:PSS):GO ratios in the HTL, where the ratio of 15:1 gave the best result with a J_{SC} of 14.9 mA/cm^2, and a V_{OC} of 0.75 V. Another reported study by Iwan et al. [119] also used GO to modify the HTL layer of both PTB7:$PC_{71}BM$ and P3HT:$PC_{61}BM$ active layer-based solar cells. The energy level diagrams of different materials used in the study, including various ratios of

[PEDOT:PSS]:GO composites, are given in Fig. 5c. A maximum PCE of 5.32% was attained using the P3HT:$PC_{61}BM$ active layer accompanied by a 1:1 ratio of [PEDOT:PSS]:GO composite HTL. The better HOMO–LUMO matching attained by addition of GO, together with enhanced hole mobility, contributed to the performance of the device. Rafique et al. [120] used [PEDOT:PSS]/GO double-decked HTL in PCDTBT:$PC_{71}BM$ (where PCDTBT is poly[N-9′-heptadecanyl-2,7-carbazole-alt-5,5-(4′,7′-di-2-thienyl-2′,1′,3′-benzothiadiazole)])-based photovoltaics, where these devices outperformed both other devices with single material HTLs made of GO and PEDOT:PSS separately, as elucidated in Fig. 5d, e, f, and g. This superior performance is attributed to primarily the work function matching between PCDTBT and [PEDOT:PSS]/GO, and then to the reduction in series resistance, which enabled better carrier mobility and charge transportation. Also, the high shunt resistance caused by GO played significant role in suppressing undesired carrier recombinations. Rafique et al. [121], in another study, treated the [PEDOT:PSS]/GO bilayer with UV radiation in the presence of ozone molecules to improve the work function and charge extraction properties, resulting in a device with PCE of 5.24%. The improved performance is also attributed to the reduction

of oxygen in GO by ozone molecules under UV irradiation, which in turn enhanced the conductivity of the HTL.

Graphene oxide can be further reduced to form reduced-graphene oxide (r-GO), which, through the reduction of oxygen species, possesses enhanced conductivity and electronic properties. Amallo et al. [122] used germanium-doped r-GO to modify the PEDOT:PSS HTL in P3HT:PCBM-based organic solar cells, attaining a PCE of 2.4%. Goumri et al. [123] enhanced the PCE of inverted solar cells based on P3HT:PCBM active layer from 2.14 to 3.06% with the addition of 3% weight of r-GO in the PEDOT:PSS HTL. Graphitic carbon nitride [124] has also been used for doping the PEDOT:PSS layer to enhance solar cell performance owing to its exceptional electronic and morphological properties. Figure 6a and b give a comparative study of reported PCEs and fill factors of different organic solar cells with nanocarbon composites as HTL materials.

Carbon nanomaterials, especially graphene and its derivatives, have proven to be effective additives to enhance the performance of polymer HTL materials like PEDOT:PSS. All the reported studies showed significant improvement in carrier mobility and charge transportation of the polymer material upon incorporation of nanocarbon materials. Most carbon nanomaterials improve the energy level alignment and reduce the number of undesired recombinations in the fabricated devices. Table 5 gives a comparison between different device structures, materials, and Solar cell parameters of different reported organic photovoltaics with nanocarbon-polymer composites as hole transport layers. Coming to the electron transport layer (ETL) of organic solar cells, the field is still dominated by materials like LiF, Ca, and PFN. The scope of polymer-nanocarbon composites is yet to be widely explored.

5 Conclusion and future prospects

Owing to cost-effectiveness, simple processing technology, mechanical flexibility, lightweightness, and extensive roll-to-roll production (R2R), the development of polymer solar cells has gained significant attention in the modern world. The tunability of optoelectronic properties in conjugated polymers by altering their molecular design opens up a wide range of scope for future energy technology. Also, nanocarbon structures like GQDs, CNTs, and graphene have a great future scope, as they are easily processable materials with exceptional properties that can be of great use for powering future technology. The next generation of photovoltaic materials will be dominated by hybrids where polymer-nanocarbon composites can play a very crucial and effective role. Incorporating nanocarbon

structures into polymers has been a proven method to enhance the performance of the active layer as well as the charge transport layer, especially the HTL of organic solar cells. These polymer-nanocarbon composites have shown superior electronic and optical properties compared to pristine polymers and nanocarbons, thus enabling enhanced performances of the fabricated devices compared to their pristine ones. Probing the exemplary properties of polymer-nanocarbon composites towards the exploration of new hybrid technologies and materials for performance enhancement in organic solar cells has a promising future outlook. As we are on the verge of transition towards the fourth generation of photovoltaics, polymer-nanocarbon composites could enable improved efficiency, mechanical strength, and cost-effectiveness. The mechanical robustness and potential for scalability and low-cost manufacturing make these hybrids appealing
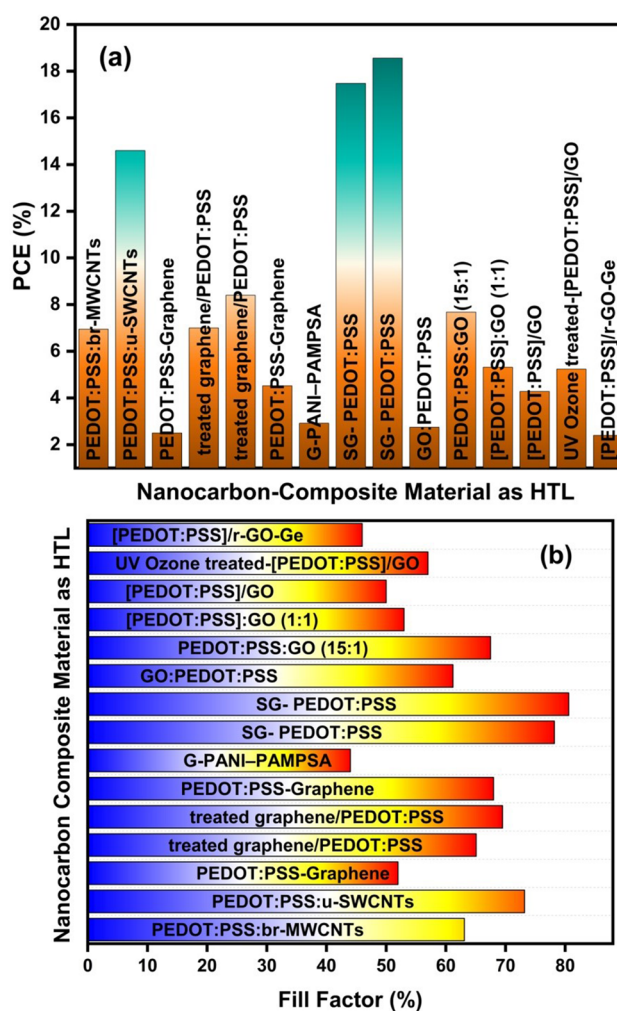

Fig. 6 Comparative study of **a** PCE and **b** fill factor of various reported organic solar cells with nanocarbon composite materials as HTL

Table 5 Comparison between different device structures, materials, and solar cell parameters of different reported organic photovoltaics with nanocarbon-polymer composites as hole transport layers

Device structure of the organics solar cells	Hybrid material used as the hole transport layer	PCE (%)	FF (%)	J_{SC} (mA/cm^2)	V_{OC} (V)	Ref
Glass/ITO/PEDOT:PSS-nGQD/ PTB7:PC$_{71}$BM/Ca/Al	PEDOT:PSS-nGQD	8.50	-	16.60	0.75	[106]
Glass/ITO/PEDOT:PSS:br-MWCNTs/ PCDTBT:PC$_{71}$BM/LiF/Al	PEDOT:PSS:br-MWCNTs	6.95	63.1	12.50	0.88	[107]
Glass/ITO/PEDOT:PSS:u-SWCNTs/PBDB-T-2F:IT-4F/PFN-Br/Al	PEDOT:PSS:u-SWCNTs	14.60	73.2	23.39	0.85	[108]
Glass/ITO/PEDOT:PSS-Graphene/ P3HT:PCBM/Al	PEDOT:PSS-graphene	2.50	52.0	8.30	0.57	[109]
Glass/ITO/treated graphene/PEDOT:PSS/ PTB:PC$_{71}$BM/ZnMgO-ZnO nano/Al	Treated graphene/PEDOT:PSS	7.00	65.1	14.30	0.75	[110]
Glass/treated graphene/PEDOT:PSS/ PTB:PC$_{71}$BM/ZnMgO-ZnO nano/Al	Treated graphene/PEDOT:PSS	8.40	69.5	16.10	0.75	[110]
Glass/ITO/PEDOT:PSS-Graphene/ P3HT:PCBM/PCBM/Al	PEDOT:PSS-graphene	4.52	68.0	13.62	0.48	[111]
Glass/ITO/G-PANI–PAMPSA/ P3HT:PC70BM/LiF/Al	G-PANI–PAMPSA	2.92	44.0	11.10	0.60	[112]
Glass/ITO/SG-PEDOT:PSS/PM6:Y6/PFN-Br/Ag	SG-PEDOT:PSS	17.48	78.2	26.58	0.84	[113]
Glass/ITO/SG-PEDOT:PSS/PM6:L8BO/ PFN-Br/Ag	SG-PEDOT:PSS	18.56	80.6	25.96	0.89	[113]
Glass/ITO/ZnO/P3HT:PC$_{71}$BM/ GO:PEDOT:PSS)/Au	GO:PEDOT:PSS	2.75	61.2	7.75	0.58	[117]
Glass/ITO/[PEDOT:PSS]:GO (15:1)/ PTB7:PCBM/PFN/Al	PEDOT:PSS:GO (15:1)	7.68	67.5	14.90	0.75	[118]
Glass/ITO/[PEDOT:PSS]:GO (1:1)/ P3HT:PC$_{61}$BM/Al	[PEDOT:PSS]:GO (1:1)	5.32	53.0	15.17	0.65	[119]
Glass/ITO/[PEDOT:PSS]/GO/ PCDTBT:PC$_{71}$BM/Al	[PEDOT:PSS]/GO	4.28	50.0	10.44	0.82	[120]
Glass/ITO/UV ozone treated-[PEDOT:PSS]/ GO/PCDTBT:PC$_{71}$BM/Al	UV ozone treated-[PEDOT:PSS]/GO	5.24	57.0	10.82	0.85	[121]
Glass/ITO/[PEDOT:PSS]/r-GO-Ge/ P3HT:PCBM/LiF/Al	[PEDOT:PSS]/r-GO-Ge	2.40	46.0	10.30	0.51	[122]

for broader applications. Leveraging the flexibility of polymers and the conductivity of nanocarbons for optimized charge transport could be a research area of high scope in the near future. Additionally, the composites offer avenues for environmental sustainability through green synthesis and recyclability. The polymer-nanocarbon hybrids present a multidimensional approach to advancing photovoltaic technology.

Polymer solar cells have improved quite quickly, yet compared to their inorganic counterparts, they still have lower power conversion efficiencies and longevity. When compared to studies on application of nanocarbon materials in perovskite and dye-sensitized solar cells, the potential of using carbon nanomaterials in organic solar cells is still a less explored field. Even though nanocarbon-polymer composites show significant improvement in device parameters, there are many limiting factors that hinder the hike in efficiency and stability of organic solar cells to a level comparable to that of their co-runners—perovskite solar cells. Several nanocarbon materials have been reported as suitable ETL and electrode materials for organic photovoltaics, but the scope of utilizing polymer-nanocarbon composites in these layers is almost left untouched.

Declarations

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