TOPICAL REVIEW

Alleviating defects in perovskites using single-walled carbon nanotubes

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Abstract

Single-walled carbon nanotubes (SWCNTs) are representative one-dimensional materials that show exceptional optical and electronic properties with various tuneable bandgaps. SWCNTs can be integrated into a variety of photovoltaics particularly, perovskite solar cells (PSCs) based on a high level of functionality and purity. In this topical review, we discuss the fundamentals of SWCNTs applied to PSCs as an electron-transporting layer, hole-transporting layer, photoactive layer, and interfacial materials from the literature. Firstly, SWCNTs in PSCs and their defect control properties improving the devices are discussed. Subsequently, electrical and morphological improvement of semiconducting SWCNT added PSCs and other types of CNTs used in PSCs are discussed chronologically. The review and discussion layout the strategies of incorporating SWCNTs within the design frame of next-generation PSCs towards the improvement of the device performance via defect passivation.

1. Introduction

Global warming and the recent energy crisis have prompted society to look towards pollution-free and renewable energy sources. Solar energy harvesting cells have drawn attention as the next-generation power generating system. Photon-to-electricity conversion efficiency is one of the most important aspects in photovoltaic devices. To enhance the efficiency, various novel materials have been utilised as electrodes, charge-transporting layers, photoactive layers, and additives in solar cells [1–6]. However, these materials have common problems of being finite, costly, and irreproducible. Researchers around the world have been searching for new materials that meet the prerequisites of eco-friendliness and industrial feasibility. Recently, nanocarbon allotropes have been reported as the materials that satisfy these demands while possessing boundless potential for additional functionalities can be infused through chemical modification. Being comprised of carbon atoms only, the nanocarbon materials, namely, fullerenes, carbon nanotubes (CNTs), and graphene exhibit a wide range of properties ranging from conductors to semiconductors depending on their electronic configurations. Moreover, their earth-abundant and mechanically resilient nature suggest a perfect replacement for conventional materials. Among these, CNTs are considered particularly promising based on the traits of being either metallic or semiconducting depending on their chirality that other nanocarbons do not possess. Furthermore, their tube-like one-dimensional (1D) structure translates to a large interfacial area with a high surface-area-to-mass ratio of \( \sim 1600 \text{ m}^2\text{g}^{-1} \) as well as their tendency to induce unique interactions with other materials [7, 8]. While multi-walled CNTs (MWCNTs) mostly behave metallic, single-walled CNTs (SWCNTs) discovered initially by Iijima [9] can be either purely metallic, purely
semiconducting, or mixture of both. The electronic properties and bandgap of SWCNTs also depend on the chirality and the tube diameter [10, 11]. Synthesised SWCNTs are generally a mixture of both semiconducting and metallic [12–15]. Semiconducting SWCNTs (S-SWCNTs) can be separated from the mixture through a purification process. The intrinsically low defect density of S-SWCNTs warrants high performance when applied to electronic devices [16]. The device application of S-SWCNTs was first reported in 1998 as the p-type metal-oxide semiconductor field-effect transistor [17]. The device application later extended further to organic solar cells where S-SWCNTs functioned as a photoactive material [18–20], a charge-transporting material [21–27], and an interfacial material [28–31]. With the emergence of perovskite solar cells (PSCs), the S-SWCNT continued to play a role in a similar manner [16, 32–34]. Incorporating S-SWCNTs into PSCs has opened the gateway to an eco-friendly, future-generation solar energy harvester, moving towards a more sustainable society.

Accordingly, there have been numerous reports on such applications where SWCNTs functioned as the electrode [35–41], photoactive material [18], the charge-transporting material [21–24, 27, 42–47], and an interfacial material [29] (figure 1). Some of the review papers nicely outline the role of SWCNTs in PSCs from the energetics perspective [32–34] as well as thermodynamic and kinetic perspectives [16]. Most importantly, addition of SWCNTs to PSCs can passivate the defect sites of the perovskite, such as lead iodide anti-sites, which suppress the charge recombination of not only the photoactive layer but other interfacial layers as reported by many researchers [19, 20, 23, 25, 31, 48]. With that being said, the perovskite community has recently focused on alleviating intrinsic defects in halide perovskites as the key strategy of improving the device efficiency and stability [49–51]. Therefore, we reviewed SWCNTs applications to PSCs from the standpoint of the defect control by categorising their functions. For SWCNTs, purity is paramount because impurity leads to charge recombination that noticeably undermines device performance [52]. Moreover, the methods of CNT production are important as there are various types of SWCNTs. For this reason, we also reviewed information regarding how and where the SWCNTs were generated and obtained by surveying every experimental section from the literature. We also identified the correlation between the PSC performance and the SWCNT materials followed by discussion linking the product quality, the methodology, and the resulting device performance.

2. SWCNTs in PSCs

2.1. SWCNTs in electron-transporting layers (ETLs)

Batmunkh and co-workers demonstrated the application of SWCNTs mixed with TiO₂ nano particles to PSCs as the ETL. n-i-p structured PSCs with a device configuration of fluorine-doped tin oxide (FTO)/compact TiO₂ (c-TiO₂)+SWCNT/mesoporous TiO₂ (mp-TiO₂)+SWCNT/CH₃NH₃PbI₃/2,2′,7,7′-tetrakis(N,N-di-p-methoxyphenylamine)-9,9′-spirobifluorene (spiro-MeOTAD)/Au were fabricated (table 1A, figure 2(a)) [21]. 1D TiO₂ nanofibers (TiO₂ NFs) were prepared by an electrospinning method. SWCNTs synthesised by the arc-discharge method were purchased from Carbon Solution Inc. (table 2A).
Table 1. Photovoltaic parameters under one sun (AM 1.5G) and structural configuration of the SWCNT-used PSCs.

| Year | Device architecture                                                                 | $J_{sc}$ (mAcm$^{-2}$) | $V_{oc}$ (V) | FF   | PCE  (%) | Reference |
|------|-------------------------------------------------------------------------------------|-------------------------|--------------|------|---------|-----------|
| A    | FTO/c-TiO$_2$+SWCNT/mp-TiO$_2$+CH$_3$NH$_3$PbI$_3$/spiro-MeOTAD/Au                  | 21.92                   | 0.98         | 0.67 | 14.03   | [21]      |
| B    | FTO/c-TiO$_2$/TiO$_2$+SWCNT/CH$_3$NH$_3$PbI$_3$/spiro-MeOTAD/Au                     | 21.96                   | 1.041        | 0.70 | 16.11   | [22]      |
| C    | FTO/c-TiO$_2$/mp-TiO$_2$+SWCNT/CH$_3$NH$_3$PbI$_3$/PTAA/Au                        | 23.6                    | 1.10         | 0.79 | 20.4    | [23]      |
| D    | FTO/c-TiO$_2$/mp-TiO$_2$+mixed SWCNT/CH$_3$NH$_3$PbI$_3$/spiro-MeOTAD/Au           | 24.59                   | 1.085        | 0.73 | 19.35   | [24]      |
| E    | FTO/SnO$_2$+SWCNT/CH$_3$NH$_3$PbI$_3$/spiro-MeOTAD/Au                              | 23.26                   | 1.12         | 0.78 | 20.33   | [25]      |
| F    | FTO/CNT-doped ZnO/CH$_3$NH$_3$PbI$_3$/spiro-MeOTAD/Au                              | 21.80                   | 1.03         | 0.69 | 15.19   | [26]      |
| G    | FTO/c-TiO$_2$/CH$_3$NH$_3$PbI$_3$/spiro-MeOTAD-SWCNT/Ag                            | 16.6                    | 1.00         | 0.58 | 9.6     | [57]      |
| H    | FTO/c-TiO$_2$/mp-TiO$_2$/CsPbI/PEI/SWCNT/Carbon                                     | 18.6                    | 0.80         | 0.71 | 10.6    | [31]      |
| I    | FTO/c-TiO$_2$/mp-TiO$_2$/CH$_3$NH$_3$PbI$_3$/spiro-MeOTAD/SCWNT-C                   | 22.36                   | 0.97         | 0.72 | 15.73   | [58]      |

The devices were compared with others incorporating double-walled CNTs (DWCNTs) and MWCNTs. The PSCs with the SWCNTs and the TiO$_2$ NF hybrid material gave a higher power conversion efficiency (PCE) of 14.03% than the PSCs using DWCNTs or MWCNTs. Such superior performance is due to high short-circuit current density ($J_{sc}$) and open-circuit voltage ($V_{oc}$) values. Successful integration of SWCNTs into TiO$_2$ NFs with the few nanometre-scale diameters provided better charge transport pathways and thus the high
Table 2. CNT information used in PSCs derived from the experimental section of each paper.

| CNT specifications and sources | Reference |
|-------------------------------|-----------|
| **ETL**                      |           |
| A Arc-discharge SWCNTs (P3-SWCNT) were purchased from Carbon Solutions Inc., Riverside, CA, USA, DWCNTs (<5 nm in diameter) and MWCNTs (<10 nm in diameter) with a purity of 90% and a length of 5–15 μm were obtained from Shenzhen Nanotech Port Co., Ltd, China. | [21] |
| B Arc-discharge SWCNTs (P3-SWCNT) were purchased from Carbon Solution Inc., Riverside, CA, USA | [22] |
| C Arc-discharge SWCNTs (P3-SWCNT) were purchased from Carbon Solution Inc., USA. | [23] |
| D Unsorted SWCNTs (Raw HiPCO, diameter 0.8–1.2 nm, length 100–1000 nm) were purchased from Nanointegr. | [24] |
| E SWCNTs purchased from Aladdin Co Ltd. | [25] |
| F Pristine CNTs purchased from Shenzhen Nanotech Port Co., Ltd. | [26] |
| **HTL**                      |           |
| G SWCNTs purchased from Sigma-Aldrich (704121-1G) | [57] |
| H SWCNTs purchased from Sigma-Aldrich (L 6–13 nm × 2.5–20 μm) | [31] |
| I Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences | [58] |
| **Photoactive layer**        |           |
| J SWCNTs purchased from Sigma-Aldrich | [18] |

$J_{SC}$ and $V_{OC}$ that the relatively thicker DWCNTs and MWCNTs could not achieve [53]. Moreover, improved energy alignment coming from the SWCNTs and TiO$_2$ NF nanohybrid is evident from the first principle density functional theory (DFT) calculation, which demonstrated that the S-SWCNTs changed their behaviour to metallic, contributing to the high $J_{SC}$ and $V_{OC}$. In addition, SWCNTs in TiO$_2$ NFs reduced the current density–applied voltage ($J$–$V$) hysteresis due to the reduced charge carrier recombination at the interface. The same group reported SWCNTs mixed with TiO$_2$ nanoparticles (TiO$_2$ NPs) and applied them to the same PSC system (table 1B, figure 2(b)) [22]. The authors used the same type of SWCNTs as the previous report (table 2B). The PSCs with the SWCNTs-TiO$_2$ NPs showed an even higher PCE of 16.11% while the pristine TiO$_2$-based PSCs gave a PCE of 13.53%. In the case of the devices using SWCNTs-TiO$_2$ NP, the $V_{OC}$ and fill factor (FF) were particularly high. As the DFT calculation suggests, even better energy alignment was achieved by using TiO$_2$ NPs and the $V_{OC}$ was improved by ~50 mV. The enhanced FF came from the improved charge transfer process, which reduced the nonradiative recombination of charge carriers as corroborated by the impedance measurement. Macdonald et al investigated the performance of arc-discharged SWCNTs (table 2C) incorporated in TiO$_2$ ETLs of PSCs with a structure of FTO/c-TiO$_2$/mp-TiO$_2$+SWCNT/CH$_3$NH$_2$PbI$_3$/poly(triaryl amine) (PTAA)/Au (table 1C, figure 2(c)) [23]. The PSCs exhibited a PCE of 20.4%, which was higher than the TiO$_2$ electrode-based reference devices which gave a PCE of 18.4%. The authors used the impedance technique and the result indicated that the addition of SWCNTs improved the recombination resistance. Interestingly, the charge transport property between the NH$_3$CH$_3$PbI$_3$-based perovskite and TiO$_2$-SWCNT did not improve dramatically compared with the TiO$_2$ only case. The added SWCNTs could passivate the electronic defect states of the TiO$_2$ and it increased the recombination resistance. In addition, the presence of the SWCNTs could trap the defect density of the TiO$_2$ and the photogeneration between the charge carriers. There have been similar strategies of reducing defects at the TiO$_2$ layer to moderate the entire recombination resistance of the tested devices [54–56]. Additionally, a substantial decrease in the saturation current density ($J_{sat}$) was observed, due to the passivation effect. This contributed to the high FF and $V_{OC}$ of the SWCNT-added devices. Bati et al employed and compared S-SWCNTs and mixed-type CNTs in TiO$_2$ ETL and investigated their effects as dopants in PSCs (table 1D) [24]. The unsorted SWCNTs were separated by the column gel chromatography method (table 2D). The mixed-type CNTs contained S-SWCNTs and metallic SWCNTs in a ratio of 2:1. The mixed CNT-added TiO$_2$ ETL-based PSCs showed the maximum PCE of 19.35%, whereas pure S-SWCNT-added devices and purely metallic SWCNT-added devices gave PCEs of 18.10% and 17.77%, respectively. The high performance of the mixed SWCNT-added devices was attributed to the presence of S-SWCNTs, which reduced the non-radiative recombination in the perovskite film. This was possible due to the intrinsic band gap of S-SWCNTs blocking the back electron transfer while metallic SWCNTs provided an excellent charge pathway for the electrons. The balanced carrier transport of electron and holes originated...
from the improved band alignment at the interface reducing the hysteresis behaviour of the device as well. This work is particularly important as it revealed that using pure S-SWCNTs is not the only answer, but a mixture of both semiconducting and metallic types synergically improves the device performance and stability. Tang et al used a hybrid material of SnO$_2$ and SWCNTs as the ETL in PSCs with a device architecture of FTO/SnO$_2$-SWCNT/CH$_3$NH$_3$PbI$_3$/spiro-MeOTAD/Au (table 1E) [25]. The SWCNTs were purchased from Aladdin Co Ltd for this work (table 2E). PSCs using the hybrid SnO$_2$-SWCNT ETL and conventional SnO$_2$ ETL exhibited PCEs of 20.33% and 17.90%, respectively. From the ultraviolet–visible absorption spectra, it can be confirmed that the SnO$_2$-SWCNT ETL has a deeper conduction band than that of SnO$_2$ ETL. This means that the SnO$_2$-SWCNT provides a larger driving force which can extract electrons with more ease from the perovskite layer. Such a large driving force led to the improved $V_{OC}$. From the space-charge-limited current, the SnO$_2$-SWCNT ETL-based devices showed a lower trap density than the SnO$_2$ ETL-based control devices. Electron mobilities of SnO$_2$ and SnO$_2$-SWCNT ETLs were found to be $2.4 \times 10^{-3}$ cm$^2$/V·s and $7.6 \times 10^{-3}$ cm$^2$/V·s, respectively. The SnO$_2$-SWCNT-added ETL exhibited higher electron mobility due to the reduced trap density and lowered charge transfer resistance possibly due to the effective passivation by SWCNTs. The device hysteresis was also successfully reduced as the hysteresis index was 14.26% for the pristine SnO$_2$ ETL-based devices while it was only 2.42% for the SnO$_2$-SWCNT-added SnO$_2$ ETL-based counterparts. Mohammed et al studied the effect of CNT-doped ZnO ETL in PSCs with a device architecture of CNT-doped ZnO/CH$_3$NH$_3$PbI$_3$/spiro-MeOTAD/Au (table 1F, figure 2(d)) [26]. When the perovskite layer was deposited on bare ZnO ETLs, the PSCs showed poor stability because the perovskite material interacted with the hydroxyl group at the surface of the ZnO ETL. The authors used CNTs purchased from Shenzhen Nanotech Port Co., Ltd to suppress the activity of the hydroxyl bonds on ZnO ETL (table 2F). The paper provides no information regarding the number of CNT walls or product type. We conjecture that the CNTs utilised were SWCNT because MWCNTs are metallic, and therefore will induce charge recombination. Albeit, the added SWCNTs were probably not purely semiconducting. The SWCNT-doped ZnO ETL also contributed to the formation of perovskite film by providing a smooth surface and enlarging the perovskite grains. The PSCs with SWCNT-doped ZnO ETL showed a PCE of 15.19%, which is higher than 9.17% of the reference devices without SWCNTs. The addition of SWCNTs reduced the carrier recombination from 29.38 ns to 17.38 ns. This was due to the improved interfacial contact between the perovskite layer and ETL, as well as reduced the trap state density in the ZnO ETL.

### 2.2. SWCNTs in hole-transporting layers (HTLs)

Miletic et al described the covalently functionalised SWCNTs for PSCs with the structure of FTO/c-TiO$_2$/CH$_3$NH$_3$PbI$_3$/spiro-MeOTAD-SWCNT/Ag (table 1G) [57]. The authors purchased SWCNTs from Sigma-Aldrich (table 2G). Covalently functionalized SWCNTs were used as a dopant for HTL to improve the chemical stability of the perovskite layer of the PSC configuration. The (7,6)-enriched SWCNTs functionalized with oligophenylenevinylene (OPV) had alkoxy groups in the central ring and amine remains in the extremities of the SWCNTs as shown in figure 3(a). The covalently functionalized SWCNTs-added PSCs showed a maximum PCE of 9.6%, and it was smaller than that of 10.9% in the Li-doped HTL device. However, the devices using SWCNTs showed improved chemical stability, confirmed by X-ray diffraction (XRD) (figure 3(a)). Yang et al demonstrated an effective strategy of incorporating polyethylene functionalized CNTs (PEI/CNTs) into PSCs as a bifunctional interlayer bridge (table 1H, figure 3(b)) [31]. The authors purchased CNTs from Sigma-Aldrich (table 2H) and the fabrication process of the PEI/CNTs is shown in figure 3(c). To investigate the effect of this interlayer bridge, CsPbI$_3$-based devices were fabricated, which displayed a PCE of 10.75% while the reference devices without the PEI/CNT interlayer showed a PCE of 7.41%. Such improvement was ascribed to the PEI/CNT bridge interlayer creating superior charge transport pathways for the excitons by forming more integrated connections between the photoactive layer and the carbon electrode. This PEI/CNT interlayer helped passivate the surface trap states in which an amino group formed the Lewis coordinate covalent bond with the Pb ions of the perovskites, reducing the charge transfer resistance. The improved interface contact and the effective passivation led to the rise in $J_{SC}$ and FF of the devices. The improved stability of the PSCs was due to the interaction between the perovskite and PEI. Accordingly, hysteresis was also reduced by the minimised defects in the perovskite thin-film. This suppressed the degradation of the device, prolonging the overall device operating time. Wang and coworkers adopted a CNT bridging method using SWCNTs as both the active layer and the electrode of PSCs, which had a device configuration of FTO/c-TiO$_2$/m-TiO$_2$/CH$_3$NH$_3$PbI$_3$/SWCNT/SCWNT-Carbon (SWCNT-C) (table 1I) [38]. The authors purchased the SWCNTs from Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences (table 2I). The CNT bridge penetrated into the interface between the perovskite and carbon electrode, and it affected the enhancement of exciton separation and carrier transport with an increase in the electrical conductivity [59] as shown in figure 3(d). The PCE of PSCs with a CNT bridge showed 15.73% and it is higher than that of the reference device without the CNT bridge with 13.86%. Furthermore, PSCs
Figure 3. (a) Preparation of OPV-decorated SWCNTs enriched in (7,6) chirality (f-SWCNT) with XRD patterns of HTM STD and HTM + f-SWCNT PSCs from 0 to 45 d stability test (rt, RH = 70%). Reprinted with permission from [57]. Copyright (2016) American Chemical Society. (b) Cross-sectional SEM image of the PSCs with PEI/CNT. (c) Synthetic route to PEI functionalized CNTs. (b), (c) Reproduced from [31] with permission from the Royal Society of Chemistry. (d) $J$–$V$ characteristics in the forward and reverse scanning direction. Reprinted with permission from [58]. Copyright (2019) American Chemical Society.

Figure 4. (a) Fabrication of S-SWCNTs with an attached ODA surfactant. (b) Top-view and cross-sectional HIM images of CNT-0, CNT-0.1, CNT-0.25, CNT-0.5. (a), (b) [18] John Wiley & Sons. © 2018 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

with the CNT bridging method presented an excellent long-term stability under severe hydrothermal conditions of $65 \pm 5\%$ relative humidity (RH) with $25 \pm 5\ ^\circ C$ and $25 \pm 5\%$ RH with $75 \pm 5\ ^\circ C$ over 90 d thanks to the hydrophobicity of the SWCNT-C layer, which prevented the intrusion of atmospheric moisture [60].

2.3. SWCNTs in photoactive layer as additives

Tiong et al synthesised octadecylamine-attached SWCNTs (ODA-SWCNTs, Sigma-Aldrich, table 2, figure 4(a)) and fabricated PSCs with a structure of FTO/c-SnO$_2$/(CH$_5$N$_2$)$_{0.85}$C$_{80.15}$Pb(1$_{0.85}$Br$_{0.15}$)$_3$-ODA-SWCNT/spiro-MeOTAD/Au (table 1, figure 4(b)) [18]. From the Raman spectra, the researchers confirmed partial conversion of the metallic SWCNTs to a semiconducting state owing to the ODA functionalization. Grain boundaries (GBs) of the perovskite films are known to possess charge traps and defects, acting as the charge carrier recombination centres. Moreover, GBs serve as the path for small molecules, such as H$_2$O and O$_2$, to intrude and instigate degradation of PSCs. Thus, reducing GBs is key to PCE improvement in PSCs. The ODA-SWCNTs could increase the grain size of the perovskite films and thereby decreasing the GBs.

During the perovskite film formation, the hydrophobic and repulsive nature of the ODA-SWCNTs decreased the number of nucleation sites and the evaporation rate of the polar solvents, such as dimethyl formamide (DMF) and dimethyl sulfoxide (DMSO). In the perspective of the device stability, the moisture penetration was hindered by the ODA-SWCNTs. The PSCs with ODA-SWCNTs showed a PCE of 16.1% with a significantly prolonged stability time compared with the devices without ODA-SWCNTs.
Table 3. Photovoltaic parameters under one sun (AM 1.5G) and structural configuration of the SWCNT-used PSCs.

| Year | Device architecture | $J_{SC}$ (mAcm$^{-2}$) | $V_{OC}$ (V) | FF | PCE (%) | Reference |
|------|---------------------|------------------------|-------------|----|---------|-----------|
|      | ETL                 |                        |             |    |         |           |
| A    | FTO/TiO$_2$:S-SWCNT/CH$_3$NH$_3$PbI$_x$Cl$_{3-x}$/S-SWCNT:P3HT/Ag | 23.52 | 0.86 | 0.71 | 14.37 | [29] |
|      | FTO/TiO$_2$:S-SWCNT/CH$_3$NH$_3$PbI$_x$Cl$_{3-x}$/P3HT/Ag | 22.85 | 0.85 | 0.70 | 13.67 |          |
|      | FTO/TiO$_2$/CH$_3$NH$_3$PbI$_x$Cl$_{3-x}$/S-SWCNT:P3HT/Ag | 21.53 | 0.80 | 0.70 | 12.07 |          |
|      | HTL                 |                        |             |    |         |           |
| B    | FTO/c-TiO$_2$/CH$_3$NH$_3$PbI$_x$/S-SWCNT/spiro-MeOTAD/Ag | 20.8 | 1.08 | 0.73 | 16.5  | [30] |
| C    | ITO/c-SnO$_2$/NH$_3$CH$_3$PbI$_x$-S-SWCNT composite/spiro-MeOTAD/Au | 23.7 | 1.14 | 0.72 | 19.5  | [19] |
| D    | ITO/SnO$_2$/NH$_3$CH$_3$PbI$_x$-S-SWCNT+DOC/spiro-MeOTAD/Au | 23.9 | 1.076 | 75.1 | 19.4  | [20] |
|      | ITO/SnO$_2$/NH$_3$CH$_3$PbI$_x$-S-SWCNT+DPB/spiro-MeOTAD/Au | 24.0 | 1.087 | 77.8 | 20.7  |          |

Table 4. Photovoltaic parameters under one sun (AM 1.5G) and structural configuration of the SWCNT-used PSCs.

| CNT specifications and sources | Reference |
|-------------------------------|-----------|
| ETL                           |           |
| A S-SWCNTs (IsoNanotubes S-99) purchased from, NanoIntegris, Canada | [29] |
| HTL                           |           |
| B CoMoCat SG65i S-SWCNTs purchased from Southwest Nanotechnologies, Inc. | [30] |
| Photoactive layer             |           |
| C High-pressure carbon monoxide processed S-SWCNTs purchased from NanoIntegris | [19] |
| D High-pressure DOC-wrapped S-SWCNTs purchased from NanoIntegris (raw soot, RO513) | [20] |

3. S-SWCNTs in PSCs

3.1. S-SWCNT in ETLs

Siva et al added S-SWCNTs to each interface of perovskite/TiO$_2$ ETL and perovskite/poly(3-hexylthiophene-2,5-diyl) (P3HT) HTL, respectively [29]. The device architecture of the fabricated solar cells was FTO/TiO$_2$:S-SWCNT/CH$_3$NH$_3$PbI$_x$Cl$_{3-x}$/S-SWCNT:P3HT/Au and the S-SWCNTs were purchased from NanoIntegris (tables 3A and 4A). In the case of the PSCs with S-SWCNT to both the ETL and HTL interfaces, the PCE was 14.47%. This is higher than that of devices with S-SWCNT added to the ETL interface only (13.67%) and to the HTL interface only (12.07%). S-SWCNTs at the interface of ETL and HTL passivated the defect sites of the perovskite film which reduced the nonradiative recombination and it increased the $V_{OC}$ and FF of the devices. The reason that S-SWCNTs could function as both the ETL and HTL was that the S-SWCNTs had the bandgap that matches that of the perovskite photoactive layer. Therefore, the nanocarbon material served as the extended version of the perovskite with higher charge mobility and minimal photoactive property.

3.2. S-SWCNTs in HTLs

Ihly et al fabricated PSCs and inserted pure S-SWCNTs (>99% semiconducting) as an interfacial contact layer between the perovskite layer and the spiro-MeOTAD HTL (table 3B, figure 5(a)) [30]. The authors purchased S-SWCNTs from Southwest Nanotechnologies, Inc. (table 4B). This CNT hybrid interfacial contact layer boosted the efficiency from 14.7% to 16.5%. The substantial increase in PCE was attributed to the insertion of S-SWCNT, which enhanced the charge transferability and reduced the electron–hole recombination. This was confirmed by the transient absorption measurement, which showed that the S-SWCNT-added interlayer extracted holes efficiently and the transferred electrons under hundreds of microseconds (figure 5(b)). Furthermore, photoelectron spectroscopy revealed that the band bending by the presence of S-SWCNT at the interfacial contact layer played a crucial role in the improvement of the charge transfer. In addition, the reduced interfacial charge accumulation minimised the hysteresis behaviour. With all of these effects combined, high $J_{SC}$ and FF led to the improvement in the PCE of the PSCs. The
3.3. S-SWCNTs in photoactive layer as additives

Seo et al used sodium deoxycholate (DOC)-attached S-SWCNTs with a semiconducting purity greater than 99.8% in the PSCs structured as the following: ITO/c-SnO\(_2\)/CH\(_3\)NH\(_3\)PbI\(_3\)-S-SWCNT/spiro-MeOTAD/Au (table 3C) [19]. S-SWCNTs with DOC was purchased from NanoIntegris and purified by Prof Kataura (table 4C). The added DOC-attached S-SWCNTs were the key material in enhancing the perovskite grain size and passivating the GBs. From the DFT calculation, the Lewis base carbonyl groups (C=O) in DOC interacted with the perovskite precursor, resulting in the S-SWCNT-DOC-PbI\(_2\) Lewis adduct. This increased the nucleation energy (\(\Delta G\)) and retarded the crystal growth, reducing the perovskite GB interfaces. Furthermore, S-SWCNTs functioned as the cross-linker between the GBs and passivated the charge defects at the GBs (figures 6(a) and (b)). The PCE of the PSCs with DOC-attached S-SWCNTs was 19.5%, and it was 1.4% higher than that of the reference devices without the additives. One year later, Lin et al reported an effective approach of enhancing the device performance by replacing the DOC surfactant with a newly designed 4,6-di(anthracen-9-yl)-1,3-phenylene bis-(dimethylcarbamate) (DPB) surfactant [20]. The authors purchased the DOC-wrapped S-SWCNTs from NanoIntegris again and the DPB was designed and synthesised by the authors themselves (table 4D). They added DPB to the S-SWCNTs and confirmed that DPB successfully replaced DOC based on the strong interaction with SWCNTs as well as the stronger degree of amphipathicity. The hydrophobic side of DPB induced stronger interaction with S-SWCNTs due to the \(\pi-\pi\) interaction and the geometry of the anthracene group matching the diameter of the S-SWCNTs perfectly. For the hydrophilic side, they attached carbamate groups that showed better miscibility with both DMF and DMSO. In addition, stronger affinity of DPB towards Pb\(^{2+}\) than that of DOC was observed through various analyses. This led to even greater interaction with the perovskite materials, which resulted in
the larger perovskite crystal grain size. In the previous report, they had found that the FF enhancement was limited, because of the inadequate passivation strength and the insulating nature of the DOC-wrapped S-SWCNTs. This time, they produced a much-improved PCE of 20.7% using the DPB-attached S-SWCNTs as compared to 19.7% of the DOC-wrapped S-SWCNT-added devices (table 3D, figure 6(c)). Such increase in the device performance was attributed mainly to the FF, which resulted from the better-aligned energy levels and improved charge transfer. This is attributed to the higher mobility of DPB, which contains conjugation of double-bonds, as well as the aforementioned stronger passivation effect. Consequently, the reduced number of trap sites improved charge carrier dynamics which is responsible for the improvement of V_{OC}. As illustrated above, the surfactants for S-SWCNTs play an unexpectedly important role in enhancing the device performance. Therefore, designing suitable surfactants give rise to the utilisation of S-SWCNTs in perovskite-based optoelectronic devices.

4. Other CNTs in PSCs

4.1. MWCNTs as either photoactive or charge transporter

Bag and coworkers reported planar heterojunction PSCs with a device architecture of ITO/PEDOT:PSS/CH_{3}NH_{2}PbI_{3}+MWCNT/[6,6]-phenyl-C_{61}-butyric acid (PC_{61}BM)/Al (table 5A) [61]. The authors purchased MWCNTs with a 40–60 nm outer diameter and 1–2 µm length (table 6A) and the fabrication image of the hexaben-zocoronene (HBC)-poly(methyl methacrylate) (PMMA)-grafted MWCNTs is shown in figure 7(a). PSCs, which were fabricated with the optimal MWCNTs concentration of 0.005% added to the perovskite layer, showed a maximum PCE of 12.9%. The addition of MWCNTs efficiently extracted the charge carriers at the interface between the perovskite and HTL, so the recombination decreased to 87% and it enhanced the V_{OC} of the devices. PSCs with MWCNTs showed the overall improvement of the V_{OC} by 70 mV while there was no effect on other parameters such as J_{SC} and FF, and the resulting PCE was 12.9%. Perovskite films, which are prepared in highly humid environments, show a rough surface, causing poor contact between the perovskite photactive layer and HTL, ultimately undermining the device performance. Cheng et al demonstrated an effective way to improve the device performance by embedding MWCNTs in the perovskite film to improve the morphology even in humid environments (table 5B) [62]. The stable dispersion of commercial MWCNTs, which were purchased from XFNANO, Inc. (table 6B), had an outer diameter of 40–60 nm and length of 1–2 µm. PSCs fabricated with MWCNTs added to the perovskite film exhibited a PCE of 11.6%, where PSCs with pristine perovskite films produced a PCE of 10.1%. MWCNTs functioned as the bridge interconnecting the perovskite grains. Those connections played the role of a hole transporter from the perovskite grains, and as a result, those generated holes were transferred from the perovskite grains to the carbon electrode. MWCNTs provide a fast charge transport pathways for the holes to travel along the tube axes, improving the charge-collection efficiency. Such enhanced charge collection reduces the carrier recombination and improves the carrier lifetime of the devices, which was confirmed by the V_{OC} decay measurement as shown in figure 7(b). Mohammed reported PSCs with a device architecture of glass/ITO/c-TiO_{2}/mp-TiO_{2}+MWCNT/1-butyl-3-methylimidazolium iodide (BMImI)-added CH_{3}NH_{2}PbI_{3}/spiro-MeOTAD/Ag (table 5C) by incorporating MWCNTs purchased from Shenzhen Nanotech Port Co. (table 6C) into the mp-TiO_{2} layer [63]. PSCs with 0.2% MWCNTs in the TiO_{2} layer resulted in a PCE of 21.7%, and it is higher than the reference devices which showed a PCE of only 12.5%. The TiO_{2}-based ETLs possessed several types of defects, such as oxygen vacancies of themselves and the defects formed by the index mismatch from the perovskite GBs. These defect sites produced the random carrier-transporting routes, resulting in the faster carrier recombination and subsequent degradation of the device performance. The MWCNTs-added TiO_{2} layers could provide the dense surface coverage and it showed the improvement in the PSC performance as the fabricated perovskite films were pinhole-free. The MWCNTs-added TiO_{2} displayed a better-aliened energy levels between ETL and the perovskite than the pristine TiO_{2} case. This was corroborated by more efficient charge carrier extraction and a greater reduction in the recombination at the interface. The MWCNT provided a superior charge transport pathways, which led to the enhancement in J_{SC} of the devices. The increase in the electron injection of the MWCNTs-added devices was revealed by external quantum efficiency (EQE) as shown in figure 7(c). Also, PSCs with the MWCNTs-added ETLs showed higher moisture and heat stability as proven by the reduced hysteresis behaviour thanks to the hydrophobicity and high thermal stability of the MWCNT. Amini et al reported two types of carbon nanomaterials, namely MWCNTs purchased from Shenzhen Nanotech Port Co. (table 6D) and graphene incorporated TiO_{2} ETL, which both were used in the fabrication of PSCs with a device architecture of ITO/c-TiO_{2}/mp-TiO_{2}+MWCNT/C_{60,0.05}((CH_{3}N_{2})_{0.83}(NH_{2}CH_{3})_{0.17})_{0.99}Pb_{2}(0.83)Br_{0.17})/spiro-MeOTAD/Ag (table 5D) [64]. The MWCNT-TiO_{2}-graphene hybrid ETL-based PSCs showed an increase in PCE of approximately 14%, which was greater than the TiO_{2}-MWCNT and TiO_{2}-graphene ETL-based devices. MWCNTs and graphene having superior electrical properties improved the charge
Table 5. Photovoltaic parameters under one sun (AM 1.5G) and structural configuration of the MWCNT-used PSCs.

| Year | Device architecture | $J_{SC}$ (mA cm$^{-2}$) | $V_{OC}$ (V) | FF | PCE (%) | Reference |
|------|---------------------|------------------------|--------------|----|---------|-----------|
| A 2016 | ITO/PEDOT:PEDOT/CH$_3$,NH$_3$PbI$_3$ + MWCNT/PC$_6$BM/Al | 18.28 | 0.97 | 72.8 | 12.91 | [61] |
| B 2016 | FTO/c-TiO$_2$/mp-TiO$_2$/mp-SiO$_2$/CH$_3$,NH$_3$PbI$_3$-MWCNT/carbon | 21.3 | 0.92 | 59 | 11.6 | [62] |
| C 2020 | Glass/FTO/c-TiO$_2$/mp-TiO$_2$/MWCNT/BM/Al | 1.085 | 27.98 | 73.25 | 21.39 | [63] |
| D 2020 | FTO/c-TiO$_2$/MWCNT-ti-TiO$_2$-graphene/C$_6$H$_5$(HN$_2$)$_0.83$(CH$_3$)$_0.17$Pb(I$_{0.83}$Br$_{0.17}$)$_3$/spiro-MeOTAD/Ag | 24.8 | 0.90 | 62.5 | 13.97 | [64] |

Table 6. CNT information used in PSCs derived from the experimental section of each paper.

| CNT specifications and sources | Reference |
|-------------------------------|-----------|
| A MWCNT (OD: 40–60 nm, Length: 1–2 µm, XFNANO, Inc.) | [61] |
| B Commercial MWCNT (OD: 30–50 nm, Length: 10–20 µm, XFNANO, Inc.) | [62] |
| C Chemical vapour deposited MWCNT (10–35 nm outer diameter) with a purity of 95% and a length of 3–10 µm were ordered from Shenzhen Nanotech Port Co. China. | [63] |
| D MWCNT (10 nm outer diameter, 97% purity from Shenzhen nanotech Port Co.) | [64] |

carrier mobility of the devices. The low-lying work function values of the graphene and CNTs between TiO$_2$ and FTO caused a reduction of the energy barrier. This improved the transportation and collection of electrons significantly as demonstrated by the increased $J_{SC}$ and elevated the device performance greatly as shown in figure 7(d).

4.2. CNTs as electrodes

The PSCs as the thin-film photovoltaics boast their advantages of being lightweight and flexible. In addition, their potential as the tandem solar cells and building-integrated photovoltaics will only be realised when the top metal electrodes are replaced by flexible, low-cost, transparent electrodes. By using the mixture of the semiconducting and metallic CNTs as the top electrode, our group demonstrated the potential of CNTs as both the cathode and the anode in PSCs (table 7A, figure 8(a)) [41]. We synthesised the CNT by using a floating-catalyst aerosol chemical vapour deposition (CVD, table 8A) and the both-CNT-electrodes-laminated PSCs showed a PCE of 7.32%. The lamination issue between the CNT and the perovskite layer was...
Table 7. Photovoltaic parameters under one sun (AM 1.5G) and structural configuration of the SWCNT-used PSCs when SWCNTs were used in electrodes.

| Year | Device architecture | $J_{sc}$ (mAcm$^{-2}$) | $V_{oc}$ (V) | FF | PCE (%) | Reference |
|------|---------------------|-------------------------|-------------|----|---------|-----------|
| A 2017 | CNT/PEDOT:PSS/CH$_3$NH$_3$PbI$_3$/PC$_{61}$BM/CNT | 15.9 | 0.80 | 0.57 | 7.32 | [41] |
| B 2019 | DWCNT/PTAA/CH$_3$NH$_3$PbI$_3$/C$_{60}$/BCP/Cu | 21.4 | 1.01 | 72.5 | 15.6 | [53] |

Figure 8. (a) Schematic illustrations of a both-CNT-electrode PSC and its energy level diagram with forward (red) and reverse (blue) bias $J–V$ curves with photovoltaic parameters and photographs of the both-CNT-electrode PSCs. Reprinted with permission from [41]. Copyright (2017) American Chemical Society. (b) Schematic illustration of a PSC structure employing solution-processed DWCNTs with SEM image, $J–V$ curves of the DWCNT-PSCs with energy diagram of the PSCs. [53] John Wiley & Sons. © 2019 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

Table 8. CNT information used in electrode of PSCs derived from the experimental section of each paper.

| CNT specifications and sources | Reference |
|-------------------------------|-----------|
| A | CNTs grown by a catalytic high-temperature CVD | [41] |
| B | DWCNT films synthesized by the aerosol CVD | [53] |

the critical point of the CNT electrode-based device research. For the improvement of the interfacial adhesion and the electron-transporting ability of the device, we used PC$_{61}$BM when laminating the CNT cathode and P3HT when laminating the CNT anode to realise fully solution-processed PSC fabrication. The PSCs with the CNT cathode showed a better performance than the PSCs with the CNT anode. Furthermore, CNT electrode-sandwiched PSCs on a plastic substrate, poly(ethylene terephthalate), displayed excellent flexibility and there was no chemical reactions observed between the perovskite layer and the plastic substrate. We also reported the application of the solution-processed DWCNT transparent electrodes for inverted PSCs (table 7B, figure 8(b)) [53]. DWCNTs that were synthesised by CVD (table 8B) [48]. HNO$_3$ and trifluoremethanesulfonic acid (TFMS) were used as the dopants that increased the electrical conductivity of the DWCNT electrodes. The pristine DWCNT device exhibited a PCE of 15.6%. However, the PCE of the HNO$_3$- and TFMS-doped DWCNT were 16.7% and 17.2%, respectively. The key factor in the device performance of the DWCNT electrode-based PSCs was the selection of right chemical dopants as well as the surface morphologies, which were governed by the tube length, dispersion state, and weight ratios of the surfactants in CNTs [65–68]. The doping effect of TFMS was higher than the HNO$_3$, because even the inner wall of the DWCNTs could be doped by the strong acid because TFMS is a super acid. The high quality of the DWCNTs separated by the surfactants meant that the individual tubes of the DWCNTs possess high conductivity due to the decrease of the Schottky CNT junction contact resistance [69]. Such works show the potential of the CNTs as electrodes not only the defect-passivating semiconductors.

5. Conclusion

In this review, we presented a summary of the past and recent progress on semiconducting CNTs being used in PSCs by not only discussing their science but also the CNT information and sources. The development of the SWCNTs as an ETL, HTL, and additives of the photoactive materials in PSCs showed the potential for further improvement of the material in near future. The alleviation and control of the defect sites in
perovskites using CNTs warrant higher PSC performance. SWCNTs in particular can reduce the charge carrier recombination by the defect control, which directly affects the PCE of PSCs. They can also function as charge carrier bridges, enhancing the carrier transport properties thanks to their high mobility and the appropriate bandgap values. With the emergence of modern industry consuming CNTs, for instance, the battery industry, the cost of CNTs is decreasing day by day. Such fields seek CNTs with better properties, which SWCNTs can provide. We project that the availability of CNTs will augment along with the growth of the market demands and the production and development of SWCNT will follow the suit.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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