Intrinsic and Extrinsic Incorporation of Indium and Single-Walled Carbon Nanotubes for Improved ZnO-Based DSSCs

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A common goal in renewable energy research is the production of semiconductor layers in a manner that is conducive to financial profitability and environmental sustainability. Important examples include the production of solar energy through the use of photovoltaics. In this work, we present a novel approach to improving the performance of DSSCs by using single-walled carbon nanotubes (SWCNT) as an extrinsic additive. The incorporation of SWCNT into the semiconductor layer of DSSCs enhances the charge transport capabilities and improves the overall efficiency of the device. This is achieved by optimizing the concentration of SWCNT and the addition of indium to the semiconductor layer. A final device utilizing 0.1 wt% SWCNT@ZnO20nm and In15Zn85O yields a current density of 16.49 mA cm⁻² and an efficiency of 4.46%.

1. Introduction

During the last decades, one of the biggest challenges of humanity has been the reduction of greenhouse gases and the implementation of green technology in all sectors of human society in order to protect and sustain our environments and health. In this context, solar cells have emerged as a promising technology to generate electricity by harnessing the power of the sun. Within the field of photovoltaics, dye-sensitized solar cells (DSSCs) are the basis for a cheap and low-temperature technology, reaching power conversion efficiencies of up to 14.6%. Traditional DSSCs consist of a wide band-gap semiconductor, typically metal oxides, deposited on top of fluorine-doped tin oxide (FTO) glass electrode. On the surface of the semiconductor a light harvesting dye is attached by a chemical anchor. A solid or liquid electrolyte, and a counter electrode coated with, for example, platinum complete the device. Over the years the working principles of DSSCs have been firmly investigated and the above mentioned key parameters have been optimized in DSSCs. Finding the right semiconductor material is one major research target besides identifying the best photosensitizing dye. Two choices of semiconductors stand out with n-type materials, such as titanium dioxide (TiO₂) and zinc oxide (ZnO), and p-type materials, like nickel oxide (NiO) or copper oxide (CuO).

Although TiO₂ still yields some of the most efficient DSSCs, ZnO electrodes have turned into a beneficial alternative. On the one hand, compared to TiO₂ electrodes, ZnO features several advantages: higher electron mobility (155 cm² V⁻¹ s⁻¹ at 300 K), a wider band gap (3.4 eV), and a simpler preparation of nanostructures. On the other hand, drawbacks of ZnO electrodes are their low stability in acidic environments and prominent electron loss processes. Electrons injected into the ZnO conduction band (CB), tend to recombine more easily with either the oxidized dye or the redox mediator when compared to electrons in the TiO₂ CBs. Another concern is the low injection yield of ZnO, which competes with intrinsic relaxation processes of the excited dye to the ground state. As a result, only moderate photocurrent efficiency (PCE) have been realized so far with current values ranging from 3.36% to 4.20%.

To tackle these drawbacks n- and p-type doping of ZnO has been performed. As a consequence, different materials, such as aluminum (η: 0.96%), gallium (η: 4.02%), and carbon...
nanotubes (CNT) (η: 2.70%),[29] copper (η: 2.03%),[30] and magnesium (η: 4.20%)[24] have been explored in an effort to reduce charge recombination losses. Especially, carbon nanotubes (CNTs) have emerged as the doping material of choice to increase the conductivity and enhance charge transport in semiconductors.[31–33] CNTs feature good conductivity and high chemical stability, which is a key incentive for their application in solar cell technologies.[32] To the best of our knowledge, simultaneous intrinsically and extrinsically concentration-dependent doping of ZnO has not been shown yet.

In this work, we report the incorporation of single-walled carbon nanotubes (SWCNTs) into the semiconductor layer of ZnO-based DSSCs. To optimize the electron injection kinetics as well as the charge collection efficiencies, on one hand, and to match the energy levels of the dye and semiconductor, on the other hand, ZnO was intrinsically modified with indium.[25] The corresponding binary indium–zinc oxide (IZO) was combined with SWCNTs, coated with a ZnO protective shell, and incorporated into DSSCs (Figure 1). IZO featuring an indium content ranging from 0 to 80 mol% was prepared via flame spray pyrolysis (see the Experimental Section), which decreases the band gap from 3.3 to 2.1 eV.[25] For the ZnO-based devices, single-layers were used and the devices were investigated by means of photophysical, electrochemical, and microscopic techniques. For the IZO-based devices, different CNT concentrations and different layer thicknesses were applied, with the objective to optimize cell performance. Important to note is that IZO-devices featuring small amounts of SWCNTs gave rise to the best figures-of-merit among all devices.

2. Results and Discussions

2.1. Optimizing ZnO using SWCNTs Featuring ZnO Shells

In the first step, we optimized the concentration of SWCNTs within ZnO films. We employed SWCNTs protected by ZnO shells of either 10 nm SWCNT@ZnO_{10nm} or 20 nm SWCNT@ZnO_{20nm} thickness, which were prepared as reported in literature.[14] To verify the presence of the ZnO shell on the SWCNT bundles and determine the layer thickness thereof we turned to scanning electron microscopy (SEM). Figure 2 corroborates that the ZnO shell covers the SWCNT bundles segmentally with a thickness of ≈10 nm for SWCNT@ZnO_{10nm} and 20 nm for SWCNT@ZnO_{20nm} (for additional images and details on the identification of ZnO see Figures S1 and S2 in the Supporting Information). Following these results, pastes with five different concentrations of SWCNT@ZnO_{10nm} or SWCNT@ZnO_{20nm} in the range from 0 to 1.5 wt% were doctor bladed onto FTO substrates. These electrodes (4 µm) were tested in a single-layer device setup featuring N719, an iodine-based electrolyte, and a platinum counter electrode (see the Experimental Section for details). Devices fabricated from pure ZnO were used as reference. Figures-of-merit and corresponding current density–voltage (J–V) curves are presented in Figure 3, as well as, Figures S3 and S4 in the Supporting Information, respectively.

The addition of 1.5 wt% SWCNT@ZnO_{10nm} reduces the open circuit voltage (V_{oc}) from 0.76 V found for the reference device to 0.7 V. At the same time, the short-circuit current density (J_{sc}) increases from 2.34 for the ZnO reference to 3.27 mA cm\(^{-2}\) for 0.1 wt% of SWCNT@ZnO_{10nm}. Beyond this point, J_{sc} steadily decreases to reach 2.92 mA cm\(^{-2}\) for 1.5 wt% SWCNT@ZnO_{10nm}. Independent from that, the fill factor (FF) initially drops from 60.8% for the ZnO reference to 51.9% for devices featuring 0.5 wt% SWCNT@ZnO_{10nm} and then grows to 59.6% in the case of the highest SWCNT@ZnO_{10nm} concentration, namely 1.5 wt%. When turning to the photocurrent efficiency (η), a similar trend as noted for the J_{sc} is observed; η increases from 1.08% for the ZnO reference to 1.37% for 0.1 wt% SWCNT@ZnO_{10nm}.

For SWCNT@ZnO_{20nm} a different trend is concluded. V_{oc} of these devices remains nearly constant at around 0.77 V for all SWCNT concentrations. J_{sc} rises from 2.34 mA cm\(^{-2}\) for the ZnO reference to 2.83 and 3.60 mA cm\(^{-2}\) for the 0.1 and 1.5 wt% SWCNT@ZnO_{20nm} devices, respectively. FFs for the SWCNT@ZnO_{20nm} devices show a more subtle trend compared to the SWCNT@ZnO_{10nm} devices with values between
58% and 61%. The efficiency $\eta$ follows the trend of the $J_{sc}$ with values of 1.08% for the ZnO reference and 1.28% for 0.1 wt% SWCNT@ZnO$_{20nm}$ as well as 1.67% for 1.5 wt% SWCNT@ZnO$_{20nm}$. These findings suggest that the highest efficiencies are obtained with 0.1 wt% SWCNT@ZnO$_{10nm}$, on the one hand, and 1.5 wt% SWCNT@ZnO$_{20nm}$, on the other hand. To relate the decrease in $V_{oc}$ to the acquired data it is important to understand what influences the open circuit voltage of a cell. $V_{oc}$ is defined as the difference between the quasi fermi-energy level of the semiconductor’s CB and the redox potential of the utilized electrolyte.$^{[35]}$ Therefore, changes regarding the redox potential of the electrolyte$^{[36]}$ or the CB energy level of the semiconductor$^{[24]}$ will ultimately change $V_{oc}$. In the current case, the decrease is explained by incorporating SWCNTs into the ZnO semiconductor. By virtue of the lower CB energy of SWCNTs relative to ZnO,$^{[37,38]}$ $V_{oc}$ is expected to drop as the SWCNT concentration is increased, which is exactly what we see. Due to the thicker ZnO shells for the SWCNT@ZnO$_{20nm}$ devices the amount of pristine SWCNT is lower, which in turn reduces the drop in $V_{oc}$ for this series.

$J_{sc}$ of a cell correlates with the number of injected and transported charges, which is reduced by recombination processes.

Figure 3. Figures-of-merit including efficiency ($\eta$), fill factor (FF), short-circuit current density ($J_{sc}$) and open circuit voltage ($V_{oc}$) for ZnO-based DSSCs featuring different amounts (wt%) of SWCNT@ZnO$_{10nm}$ (left) and SWCNT@ZnO$_{20nm}$ (right).
across the different interfaces within the cell.\cite{39,40} Therefore, any attempts to enhance charge injection and facilitate transport or to hamper charge recombination should increase $J_{sc}$. In the case of SWCNT@ZnO, the noted increase in $J_{sc}$ is likely to be a combination of both alterations. First, the higher conductivity of the SWCNTs and the lower lying CB should boost the charge injection and transport.\cite{41-43} Second, the ZnO should hamper the recombination with the electrolyte due to a higher CB of ZnO. The results observed for $J_{sc}$ corroborate this hypothesis. For FF and $\eta$ of measured devices the values are calculated according to the following equations

$$\text{FF} = \frac{V_{\text{MPP}} \times J_{\text{MPP}}}{P_{\text{light}}}$$

$$\eta = \frac{V_{\text{MPP}} \times J_{\text{MPP}}}{P_{\text{light}}} \times 100$$

where $V_{\text{MPP}}$ is the voltage at the maximum power point, $J_{\text{MPP}}$ is the current density at the maximum power point, and $P_{\text{light}}$ is the power of incident light, which is 100 mW cm$^{-2}$.\cite{44} Large increases in only $V_{oc}$ or $J_{sc}$ will lead to a reduction in FF. Additionally, shunt and series resistances play an important role in the case of FF but will only be mentioned briefly here. In the case of $\eta$, it is entirely dependent on the maximum power point. As such, changes in $V_{oc}$ and $J_{sc}$ govern $\eta$, although FF is known to play an important role as well. In terms of FF a slight drop is noted after SWCNT addition, which correlates with the increase in $J_{sc}$. However, as mentioned earlier, the increase in $J_{sc}$ is likely to be a combination of both alterations.

The impact in the case of the SWCNT@ZnO 10nm is somehow different. Relative to the ZnO reference, $R_w$ and $R_k$ rise at 0.1 wt% SWCNT@ZnO 10nm. From here on, $R_w$ and $R_k$ drop steadily to values that are lower than those seen for the ZnO reference. $\tau$ increases from 320 to 370 ms for the same concentrations.

**Figure 4.** Calculated EIS data including collection efficiency ($\eta_{\text{coll}}$), effective charge-carrier diffusion length ($L_{\text{eff}}$), electron lifetime ($\tau$), dark resistance ($R_k$), and light resistance ($R_w$) for ZnO-based DSSCs (N719 dye) featuring different amounts (wt%) of SWCNT@ZnO 10nm (left) and SWCNT@ZnO 20nm (right).
stays constant at around 0.75 ms up to a SWCNT@ZnO\textsubscript{20nm} concentration of 1.0 wt%, but rises afterwards to 0.91 ms. \( L\text{eff} \) follows the same – albeit weaker – tendency as noted for SWCNT@ZnO\textsubscript{10nm}. For 0.1 wt% SWCNT@ZnO\textsubscript{20nm}, it initially decreases, yet for concentrations exceeding 0.1 wt% \( L\text{eff} \) is enlarged until it reaches 0.73 \( \mu \)m at the highest concentration. \( \eta\text{coll} \) and \( J\text{sc} \) go hand-in-hand, that is, revealing two maxima at 0.1 and 1.5 wt% SWCNT@ZnO\textsubscript{20nm} with 32%, and 36%, respectively. The subtle increase in \( R\text{w} \) at low SWCNT@ZnO\textsubscript{20nm} concentrations seems to be out of line at first. However, the increase in \( R\text{k} \) and the fact that it is significantly larger than \( R\text{w} \) prompts to the unlikelihood of recombination. The subsequent reduction of both resistances with increasing concentration keeps \( R\text{k} \) larger than \( R\text{w} \) and, in turn, improves charge transport. This is reflected in the rise in \( \eta\text{coll} \) and \( J\text{sc} \).

In the case of the thicker ZnO shells, which surround the SWCNTs, the improvement in \( L\text{eff} \) as well as \( \tau \) is only observable for higher concentrations. Due to the nature of the sample, the pure CNT weight cannot be precisely determined. Therefore, less SWCNT is present in these layers, meaning higher concentrations are needed to see the same effects as for SWCNT@ZnO\textsubscript{10nm}.

Both series clearly indicate that \( \eta\text{coll} \) for ZnO-based devices is far from optimum. An immediate consequence is the moderate efficiency, which is typically reported for such devices.\cite{46}

In order to overcome the “\( \eta\text{coll} \)” bottleneck, we revisited our previous study of incorporating indium into ZnO, with the goal to match the band gap of the semiconductor with that of N719.\cite{25}

Our previous studies have documented that a systematic lowering of the quasi Fermi energy level by means of variable indium-containing ZnOs (IZOs) is a successful approach to match the energy levels within DSSCs.

With the spray pyrolysed IZO, a batch-to-batch optimization is necessary to accurately match the dye and semiconductor energy levels. In addition, we checked the IZO and compared our results with values already published in the literature.\cite{25} The obtained data matched the expected results nicely – Figures S15 and S16 in the Supporting Information.

2.2. Optimizing ZnO using Indium and SWCNTs

In the second step, previous measurements were taken into account to disclose any synergetic effects: SWCNT@ZnO\textsubscript{10nm} and SWCNT@ZnO\textsubscript{20nm} were employed at the best performing concentration, namely 0.1 and 1.5 wt%, respectively, and incorporated into single- (3 \( \mu \)m), double- (5.8 \( \mu \)m), and triple-layer (9 \( \mu \)m) devices featuring In\textsubscript{15}Zn\textsubscript{85}O. To verify the presence of SWCNTs within the semiconducting IZO we turned to microscopic studies and recorded both atomic force

**Figure 5.** AFM images of IZO with SWCNT@ZnO\textsubscript{20nm} at 1.5 wt% concentration with a zoom-in onto the CNT on the right side (height of the CNT is around 50 nm).

**Figure 6.** AFM images of 15 mol% IZO layers with 0 wt% (left), 0.1 wt% (middle), and 1.5 wt% (right) of SWCNT@ZnO\textsubscript{20nm}.
microscopy (AFM) and SEM images. Exemplary AFM images of single-layers of IZO featuring 1.5 wt% SWCNT@ZnO20nm are presented in Figure 5. SWCNTs, which merged into the semiconductor layer, are clearly discernible in both images. Additional images (Figure 6 and Table 1) revealed the surface roughness at different concentrations of SWCNT@ZnO20nm, that is, 0, 0.1, and 1.5 wt%. From these images it is evident that the layer roughness decreases with the SWCNT@ZnO20nm concentration. It is likely that this relates to the sintering process, during which IZO not only attaches to the FTO surface, but also to the ZnO shells of SWCNTs.[34,47] To further prove the presence and incorporation of SWCNTs into IZO we turned to SEM studies. For both SWCNT@ZnO10nm and SWCNT@ZnO20nm the images in Figure 2c,f, respectively, confirm the presence of both types of SWCNTs. In accordance with the AFM images, IZO appears as a homogeneous nanoporous layer featuring good connectivity between the ZnO shells and the bulk material.

Next, we continued with the construction of DSSC devices featuring both IZO and SWCNT.

Figure 7 shows the J–V curves measured for the SWCNT@ZnO10nm and SWCNT@ZnO20nm devices. For the SWCNT@ZnO10nm and SWCNT@ZnO20nm cells featuring 0.1 wt% SWCNTs, similar trends are observed for the figures-of-merit presented – Figure 8. A Voc decrease from 0.76 V for the ZnO reference is present upon SWCNT addition and increasing layer thickness. For example, the values for SWCNT@ZnO10nm and SWCNT@ZnO20nm are 0.59 and 0.60 V, respectively. At the same time, Jsc is augmented to 13.54 mA cm\(^{-2}\) for the SWCNT@ZnO10nm triple-layer cells and 16.59 mA cm\(^{-2}\) in the case of SWCNT@ZnO20nm.

Noteworthy is that the Jsc of the triple-layer device featuring SWCNT@ZnO10nm is slightly lower than the double-layer devices with a value of 13.94 mA cm\(^{-2}\). The FF shows a slight decline for all devices, especially noticeable for thicker layers. The only exception is the SWCNT@ZnO10nm triple-layer cell yielding the highest FF of 53%. A significant jump is seen for the η of the cells when going from single- to double-layer cells. This is followed by a more elusive jump for the triple-layer cells. To be exact, η values reach 4.21% for SWCNT@ZnO10nm and 4.46% for SWCNT@ZnO20nm. Changes in Voc are explained through incorporation of SWCNTs and the increase in surface trap states, especially within thicker layers. Such surface trap states lead to an increase in recombination with the electrolyte.

### Table 1. Listed values of measured devices featuring single, double, and triple-layer devices for 1.5 wt% SWCNT@ZnO10nm, and SWCNT@ZnO20nm.

| SWCNT@ZnO20nm [wt%] | Roughness [nm] | Peak-to-valley [nm] |
|----------------------|---------------|---------------------|
| 0                    | 107.6         | 489.1               |
| 0.1                  | 45.9          | 289.3               |
| 1.5                  | 26.4          | 206.0               |

Figure 7. J–V characteristics for DSSCs (N719 dye) featuring a ZnO reference (black), In\(_{15}\)Zn\(_{85}\)O (IZO) single- (ML; red), In\(_{15}\)Zn\(_{85}\)O (IZO) double- (DL; green), and In\(_{15}\)Zn\(_{85}\)O (IZO) triple-layer (TL; blue) with 0.1 wt% SWCNT@ZnO10nm (top left) and SWCNT@ZnO20nm (top right) as well as single- (ML; brown), double- (DL; dark-green), and triple-layer (TL; cyan) with 1.5 wt% SWCNT@ZnO10nm (bottom left) and SWCNT@ZnO20nm, (bottom right).
and, therefore, to a lowering of $V_{oc}$. The boost in $J_{sc}$ stems mainly from the SWCNT incorporation as discussed above as well as the thicker layers. Due to the mesoporous structure of the semiconductor layers an increase in thickness results in a magnification of absorption sites within the layers. This results in an overall higher dye loading, which directly increases $J_{sc}$ of the device. For the FF a slight decline is observed, which stems from the $J_{sc}$ increases as proven in Equation 1. $\eta$ unsurprisingly follows a very similar trend as the $J_{sc}$. The increase in $J_{sc}$ leads to up-shifting of the maximum power point. According to Equation 2, this increases $\eta$.

In a direct comparison, triple-layer cells utilizing SWCNT@ZnO20nm give rise to a 6% improved power-conversion-efficiency compared to those with SWCNT@ZnO 10nm. Here, the corresponding $\eta$s are 4.46% and 4.21%.

Similar trends evolve at higher concentrations of 1.5 wt% – Figure 9. With increasing layer thickness, $V_{oc}$ decreases, which is more pronounced for SWCNT@ZnO10nm than for SWCNT@ZnO20nm. The thinner ZnO shell is likely to be responsible here. As the semiconductor layers get thicker and thicker, higher $J_{sc}$s are recorded. Mono-layer devices show a similar 10.7 mA cm$^{-2}$, while thicker layers of SWCNT@ZnO20nm yield 16.21 mA cm$^{-2}$ compared to 15.27 mA cm$^{-2}$ for layers of SWCNT@ZnO10nm. For the higher SWCNT concentration FFs remain nearly constant throughout our assays: 50% for SWCNT@ZnO10nm and 46% for SWCNT@ZnO20nm. For the triple-layer devices the highest $\eta$s are 4.13% and 4.54% for SWCNT@ZnO10nm and SWCNT@ZnO20nm, respectively.

To gain further insights into the effects that the incorporation of SWCNTs into IZO has, we probed the devices by means of EIS. All measured and calculated data for the $J$–$V$ and EIS measurements are shown in Figure 8 and Table S1 (Supporting Information) for 0.1 wt% SWCNT and in Figure 9 and Table S2 (Supporting Information) for 1.5 wt% SWCNT. Comparing the EIS data for 0.1 and 1.5 wt% SWCNTs, the only significant difference, which is discernable, is that for $\tau$. At first glance, both concentrations exhibit similar trends. $R_k$ as well as $R_w$ decrease for thicker layers. In the low SWCNT concentration regime $R_k$ drops from 106 to 56.2 $\Omega$ for SWCNT@ZnO10nm and from 92.1 to 62.9 $\Omega$ for SWCNT@ZnO20nm. $R_w$ shows a comparable behavior with values decreasing from 49.4 to 22.2 $\Omega$ and from 44.9 to 23.7 $\Omega$, respectively. For $\tau$ the values of the SWCNT@ZnO20nm devices increase from 4.3 to 77 ms with layer thickness. In the case of SWCNT@ZnO10nm devices, however, a different picture evolves. Here, the corresponding values are 4.3 ms for single-layers, 6.4 ms for the double-layers, and 5.2 ms for the triple-layers.

Looking at the $L_{eff}$ a linear dependency is observed at low SWCNT concentrations. Values rise from 1.3 to 4.3 $\mu$m and from 1.2 to 5.1 $\mu$m for SWCNT@ZnO10nm and SWCNT@ZnO20nm, respectively. Finally, $\eta_{coll}$ increases as a function of the layer number with values that start at 53.4% and end at 60.5% for SWCNT@ZnO10nm and from 92.1 to 62.9 $\Omega$ for SWCNT@ZnO20nm. $R_w$ shows a comparable behavior with values decreasing from 49.4 to 22.2 $\Omega$ and from 44.9 to 23.7 $\Omega$, respectively. For $\tau$ the values of the SWCNT@ZnO20nm devices increase from 4.3 to 77 ms with layer thickness. In the case of SWCNT@ZnO10nm devices, however, a different picture evolves. Here, the corresponding values are 4.3 ms for single-layers, 6.4 ms for the double-layers, and 5.2 ms for the triple-layers.

Figure 8. Figures-of-merit including efficiency ($\eta$), fill factor (FF), short-circuit current density ($J_{sc}$), and open circuit voltage ($V_{oc}$) for DSSCs (N719 dye) featuring different numbers of I$_{15}$Zn$_{85}$O (IZO) layers as well as SWCNT@ZnO$_{20nm}$ (black) and SWCNT@ZnO$_{10nm}$ (red) at concentrations of 0.1 wt% (left) and 1.5 wt% (right).
for SWCNT@ZnO\textsubscript{20nm}. For the final two parameters, $L_{\text{eff}}$ and $\eta_{\text{coll}}$, SWCNT@ZnO\textsubscript{10nm} devices show slightly larger values than SWCNT@ZnO\textsubscript{20nm} devices.

Considering our EIS findings the $R_k$ decrease implies less hindered charge recombination for thicker layered-devices. This is not surprising as thicker layers result in more surface trap states, which, in turn, increase the probability of recombination with the electrolyte. However, the simultaneous decrease in $R_k$ implies a better charge transfer. This mainly stems from the SWCNT incorporation into the IZO semiconductor as it generates highly conductive channels. This is verified by the increase in $J_{sc}$ as well as $\eta$. More layers result in an increase in both $L_{\text{eff}}$ and $\tau$ due to the need for electrons to travel longer distances to reach the electrode back contacts, which is observed. Finally, better $\eta_{\text{coll}}$ indicates a superior charge collection and, as such, documents the success of our work. All of our devices perform much better than devices made with conventional ZnO, which yielded 1.08% as a reference point. By modifying ZnO intrinsically with 15 mol\% indium and extrinsically with 0.1 wt\% SWCNT efficiencies of 4.13\% for SWCNT@ZnO\textsubscript{10nm} and 4.46\% for SWCNT@ZnO\textsubscript{20nm} were determined. Considering that the largest $J_{sc}$ emerged in the case of the triple-layer devices featuring 0.1 wt\% of SWCNT@ZnO\textsubscript{20nm}, we, thus, conclude that low SWCNT concentrations are already the best choice in terms of thick layer performance.

### 3. Conclusions

In the first step, the incorporation of SWCNTs into layers of different ZnO-based semiconductors offers desirable advantages in terms of improving DSSCs. This work utilized SWCNTs outfitted with a 10 nm (SWCNT@ZnO\textsubscript{10nm}) and 20 nm (SWCNT@ZnO\textsubscript{20nm}) thick shell of ZnO. The incorporation of these SWCNTs into ZnO-based electrodes resulted in longer $\tau$ and higher $\eta_{\text{coll}}$ due to reduced recombination and better charge transport. This yielded boosted $J_{sc}$s with only a slightly negative impact on the $V_{oc}$ owing to the lower CB level of the SWCNTs. Overall $\eta$s for these devices ranged from 1.08\% for just plain ZnO to 1.37\% and 1.67\% in the presence of 0.1 wt\% of either SWCNT@ZnO\textsubscript{10nm} or SWCNT@ZnO\textsubscript{20nm}, respectively.

In the next step zinc in ZnO was replaced by indium to improve the $J_{sc}$s and $\eta_{\text{coll}}$s as well as to adjust the energy levels of dye and semiconductor. A ratio of 15 mol\% indium to 85 mol\% zinc in In\textsubscript{15}Zn\textsubscript{85}O was found to be the optimum, yielding a $J_{sc}$ of 9.81 mA cm\textsuperscript{-2} and $\eta$ of 3.66\% relative to 2.34 mA cm\textsuperscript{-2} and 1.08\% for bare ZnO. In the final step, SWCNT@ZnO\textsubscript{10nm} and SWCNT@ZnO\textsubscript{20nm} were integrated into IZO-based DSSCs featuring In\textsubscript{15}Zn\textsubscript{85}O. Here, the effects from the presence of SWCNT shows their full potential as the charge transport and collection efficiency were largely facilitated in the In\textsubscript{15}Zn\textsubscript{85}O films, improving the cells figures-of-merit. To this end, $J_{sc}$ increases from 2.34 mA cm\textsuperscript{-2} for pure ZnO to 16.59 mA cm\textsuperscript{-2} for triple-layer devices featuring In\textsubscript{15}Zn\textsubscript{85}O and 0.1 wt\% of SWCNT@ZnO\textsubscript{20nm}. This results in a quadrupling of efficiencies to 4.46\% when compared to the ZnO reference. Future investigations will focus on further optimizing the dye and electrolyte of these devices, as well as, the cell architecture.

### 4. Experimental Section

**Device Fabrication Materials:** Ethanol (Roth), acetonitrile (Roth), tetrahydrofuran (Sigma-Aldrich) isopropanol (Sigma-Aldrich), and
valeronitrile (Alfa Aesar) were used in HPLC grade and without further purification. For the synthesis of the indium-doped ZnO nanopowders zinc acetylacetonate hydrate, 2-methoxyethanol (≥99.5%), acetic acid, and ethanolamine were purchased from Sigma-Aldrich. Indium acetate (99.99%) was obtained from Alfa Aesar. To prepare the electrolyte 1,2-dimethyl-3-propylimidazolium iodide (Sigma-Aldrich), resublimed iodine (Merck), lithium iodine (Sigma-Aldrich), and 4-tert-butylpyridine (Sigma-Aldrich) were used. For the counter electrodes a solution of H$_2$PtCl$_6$ (~38 wt% Pt concentration, Sigma-Aldrich) in isopropanol was utilized. FTO-glass substrates, 3.2 mm, 8 Ω cm$^{-2}$ were acquired from XOP glass. The N719 dye was purchased from Solaronix.

**IZO Nanopowder Synthesis:** Stock solution A (zinc acetylacetonate hydrate, acetic acid in 2-methoxyethanol) and B (indium acetate, ethanolamine in 2-methoxyethanol) were sonicated for 15 min before mixing. The precursor solution was heated to 70 °C and stirred for 15 min until a clear solution was obtained. The solution was then spray ignited (5 mL min$^{-1}$; dispersion gas: O$_2$, 5 L min$^{-1}$; 1.5 bar) and evaporated by a stoichiometric CH$_3$OH (3 L min$^{-1}$)/O$_2$(1.5 L min$^{-1}$) flame. The resulting nanopowders were filtered and vacuum dried on a polyimide membrane filter. A detailed description of this standard process is given by Kunzmann et al.$^{[5]a}$ and a description of the burner by Engel et al.$^{[5]f}$

**Device Fabrication and Characterization:** FTO substrates were cleaned by a standard procedure immersing the slides subsequently into solutions of acetone, detergent (deconex FPD 120, 1% vol. solution in 150 mL deionized water), pure deionized water, and isopropanol. The solutions were sonicated for 15 min each (Elma, Elmasonic P), and finally the substrates were dried under a nitrogen flow. To cleanse the slides were hand shaking to minimize the mechanical peel-off of ZnO shell and then drop-casted on silicon wafer substrates to obtain the SEM images except for Figure 2c,f, by which the samples were prepared according to the described procedure above. The SEM experiments were conducted on a Delta-SEM (Demonstrator, Carl Zeiss Microscopy, Germany) with 1 keV primary beam energy and a working distance of 3 mm.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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**Conflict of Interest**

The authors declare no conflict of interest.

**Data Availability Statement**

The data that support the findings of this study are available from the corresponding author upon reasonable request.

**Keywords**

indium–zinc oxide photoanodes, n-type DSSCs, semiconductor doping, single-wall carbon nanotubes

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