Multifunctional CNT:TiO₂ additives in spiro-OMeTAD layer for highly efficient and stable perovskite solar cells

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Abstract
Hole transport layer (HTL) is very important for the power conversion efficiency (PCE) and stability of perovskite solar cells (PSCs). As current state-of-the-art HTL, Li-TFSI doped spiro-OMeTAD often suffers low conductivity and the hydrolysis of the additive Li-TFSI, which significantly hinders the further improvement of PCE of PSCs. Besides, conventional spiro-OMeTAD has no functional of directly passivating the perovskite crystal defects. Herein, multifunctional TiO₂ nanoparticles (NPs)-modified CNT (CNT:TiO₂) doped spiro-OMeTAD (spiro-OMeTAD+CNT:TiO₂) HTL is reported for the first time. The incorporated CNT:TiO₂ not only significantly increases the conductivity of spiro-OMeTAD+CNT:TiO₂, but also effectively passivates the crystal defects of perovskite layer. The optimized PSCs with spiro-OMeTAD+CNT:TiO₂ HTL achieved a peak PCE of 21.53%, much higher than that (17.90%) of the conventional spiro-OMeTAD based PSCs and also show significantly improved stability.

KEYWORDS
additive, carbon nanotube, multifunctional, perovskite solar cells, spiro-OMeTAD

1 | INTRODUCTION

Since the seminal work in 2009,¹ perovskite solar cells (PSCs) based on organic-inorganic halide perovskite ABX₃ (A = CH₃NH₃⁺, Cs⁺;²-⁵ B=S n²⁺, Pb²⁺;⁶,⁷ X=Cl⁻, I⁻, Br⁻;⁸-¹¹) have shown a dramatic increase in power conversion efficiency (PCE) from the initial 3.8% PCE to the currently certified 25.5% PCE,¹² which makes them comparable to the PCE of polycrystalline silicon solar cells. At present, PSCs can be classified into three types according to their architectures, namely, planar heterojunction, mesoscopic heterojunction, and bulk heterojunction architectures. A typical planar heterojunction PSC is formed by sandwiching a perovskite active layer between a hole transport layer (HTL) and an electron transport layer (ETL).

The HTL serves to extract photogenerated hole from the perovskite layer and plays an important role in preventing charge recombination at the metallic electrode, maximizing charge transfer efficiency, and improving the stability by preventing moisture/oxygen from contacting perovskite film. So far, many kinds of HTLs have been implemented in PSCs including spiro-OMeTAD, PTAA,¹³ P3HT,¹⁴ CuSCN,¹⁵ CuInS₂.¹⁶ Qiang Lou and Huilin Li have the same contributions.
NiO, and so forth. Among these HTLs, spiro-OMeTAD is the most widely used HTL so far. However, pristine spiro-OMeTAD film suffers from serious drawbacks including low conductivity and poor compactness, which disfavors charge transport and also cannot effectively prevent oxygen and moisture from permeating into perovskite layer due to the pinholes and cracks of the spiro-OMeTAD film, thus leading to charge recombination and a deterioration of device performance. To enhance the electrical conductivity of spiro-OMeTAD, additives and/or dopants such as alkaline-earth bis(trifluoromethanesulfonimide) have been added to spiro-OMeTAD. Typical additives are Li-TFSI and TBP, which act as oxidizing dopants to improve hole mobility of spiro-OMeTAD. However, the Li-TFSI is deliquescent and hygroscopic that absorbs water and enhances the agglomerative properties of Li-TFSI, which gravely degrades the HTL as well as the perovskite film. Meanwhile, the TBP can also degrade perovskite film due to the formation of a \( [\text{PbI}_2\square\text{TBP}] \) coordinated complex. The inclusion of Li-TFSI and TBP further accelerates infiltration of moisture/oxygen into perovskite layers and can gravely degrade the perovskite materials, thus accelerating the degradation of PSCs. In addition to these, the spiro-OMeTAD does not have the ability to passivate the perovskite defect state at the perovskite/HTL interface.

Therefore, it may be an effective solution to overcome these shortcomings of spiro-OMeTAD by incorporating a multifunctional material into spiro-OMeTAD. Carbon-based doping materials may be the best candidates because they do not react with halides and are inherently stable and hydrophobic. Typically, single-walled carbon nanotube (CNT) and graphene oxide (GO) have been used as additives in spiro-OMeTAD layer to enhance the efficiency and stability of PSCs. Unfortunately, the doping CNT mainly enhances the conductivity of the spiro-OMeTAD film and has no passionation effect on perovskite defects. In order to overcome these problems, the strategy of functionalizing CNT with modifiers has been tried recently. For example, an organic modifier, octadecylamine, is used to functionalizeCNTs onto the surface of the perovskite layer for PSCs. Previous studies on inorganic TiO\(_2\)-modified CNT show that a semiconductor heterojunction can be formed through the interaction between TiO\(_2\) and highly active carbon atoms of CNT, which may improve the conductivity of CNT:T\(i\)O\(_2\) composite and reduce charge recombination. Considering these advantages of CNT:T\(i\)O\(_2\) composites, in this study, TiO\(_2\) NPs modified single-walled CNT (CNT:T\(i\)O\(_2\)) are added to spiro-OMeTAD layer as additives for the first time to further improve the PCE and stability of CH\(_3\)NH\(_3\)PbI\(_3\)-based PSCs with spiro-OMeTAD HTL. The structure and energy levels of prepared PSCs are shown in Figure 1. Our results demonstrate that both CNT and CNT:T\(i\)O\(_2\) improved the PCE and stability of the PSCs. More importantly, compared with pure CNT, the CNT:T\(i\)O\(_2\) can improve the mobility of holes in spiro-OMeTAD layer more effectively, thus making the hole extraction at the CH\(_3\)NH\(_3\)PbI\(_3\)/spiro-OMeTAD interface more effective. Besides, CNT:T\(i\)O\(_2\) may directly passivate the perovskite crystal defects and further improve the hydrophobicity of the spiro-OMeTAD+CNT:T\(i\)O\(_2\) composite HTL. The hydrophobicity of the CNT:T\(i\)O\(_2\) also makes the device performance more stable. As a result, these multiple functions of the doping CNT:T\(i\)O\(_2\) greatly improve the efficiency and stability of the PSCs.

## RESULTS AND DISCUSSION

The morphology and structure characterization of CNT:TiO\(_2\) are shown in Figure S1a, from which it can be clearly observed that individual TiO\(_2\) NPs are deposited on the CNTs with an average diameter of 10 nm. Figure S1b shows the HR-TEM image of deposited TiO\(_2\) NPs with diameters of ~6 nm, from which the lattice fringes of 0.235 nm correspond to the (001) plane of anatase TiO\(_2\), confirming the formation of TiO\(_2\) NPs on the CNT. Figure 2A shows the top-view SEM image of spiro-OMeTAD layer on the top of as-prepared CH\(_3\)NH\(_3\)PbI\(_3\) film, from which many pinholes are observed. These pinholes may cause serious problems. On the one hand, the gold electrode material may directly contact the perovskite layer through these holes during the evaporation process to form dark-state leakage current; on the other hand, moisture and oxygen in the surrounding environment may penetrate into the perovskite layer through these holes, causing the degradation of the perovskite material. Figure 2B and C show top-view SEM images of spiro-OMeTAD+CNT (0.025 and 0.10 mg mL\(^{-1}\)) and spiro-OMeTAD+CNT:T\(i\)O\(_2\) (0.025 and 0.10 mg mL\(^{-1}\)) HTLs, respectively. The insets in Figure 2B and C show that, when the concentration (0.025 mg mL\(^{-1}\)) of CNT and CNT:T\(i\)O\(_2\) powders is low, CNT and CNT:T\(i\)O\(_2\) are not easily observed in spiro-OMeTAD matrix. When the concentration is further increased (0.10 mg mL\(^{-1}\)), the dispersed CNT and CNT:T\(i\)O\(_2\) are clearly observed. Furthermore, by doping CNT and CNT:T\(i\)O\(_2\) into the spiro-OMeTAD matrix, the pores in the spiro-OMeTAD almost disappear and the evenly distributed CNT and CNT:T\(i\)O\(_2\) are clearly visible, indicating that the CNT material can effectively improve the compactness of the spiro-OMeTAD layer. At the same time, considering the high conductivity of carbon materials, doped carbon nanotubes are expected to effectively improve the
conductivity of holes in the spiro layer. Figure 2D, E, and F show cross-section SEM images of the FTO/cp-TiO2/mp-TiO2/CH3NH3PbI3/spiro-OMeTAD, FTO/cp-TiO2/mp-TiO2/CH3NH3PbI3/spiro-OMeTAD+CNT, and FTO/cp-TiO2/mp-TiO2/CH3NH3PbI3/spiro-OMeTAD+CNT:TiO2 films, respectively. The thickness of CH3NH3PbI3 layer is about 290 nm, which is consistent with the active layer thickness of high efficiency solar cells reported earlier. Compared with that (120 nm) of spiro-OMeTAD layer, the thickness increased slightly to 136 and 148 nm for spiro-OMeTAD+CNT and spiro-OMeTAD+CNT:TiO2, respectively.

To determine the electronic properties of the doping spiro-OMeTAD (ie, spiro-OMeTAD+CNT and spiro-OMeTAD+CNT:TiO2), the combined UV-vis spectrum and UPS measurements are performed, as shown in Figure 3. Figure 3A shows that both spiro-OMeTAD+CNT and spiro-OMeTAD+CNT:TiO2 films absorb mainly the light with a wavelength of less than 450 nm. Furthermore, the inset of Figure 3A shows that the Wide bandgap ($E_g$) is 2.92 and 2.96 eV for spiro-OMeTAD and spiro-OMeTAD+CNT:TiO2 films, respectively. Figure 3B displays the UPS spectra of the spiro-OMeTAD films with CNT and CNT:TiO2. The valence-band energy level ($E_v$) can be obtained from the UPS spectra by the following equations $W_s = h\nu - E_{cutoff}$ and $E_v = 21.20 - (E_{cutoff} - E_{onset})$ (inset in Figure 3B), which is $-5.10$ and $-5.15$ eV for the spiro-OMeTAD+CNT and spiro-OMeTAD+CNT:TiO2 films, respectively. Therefore, the incorporated CNT significantly increased the $E_v$ of the HTL (ie, spiro-OMeTAD+CNT) because of the high work function of CNT. However, by...
incorporating CNT:TiO$_2$, the $E_v$ of the spiro-OMeTAD +CNT:TiO$_2$ decreases to $-5.15$ from $-5.10$ eV, which is closer to the $E_v$ of perovskite layer compared with that ($-5.10$ eV) of the spiro-OMeTAD+CNT. Therefore, compared with spiro-OMeTAD+CNT HTL, the spiro-OMeTAD+CNT:TiO$_2$ HTL would be more conducive to the hole transfer from perovskite to HTL and optimize the valence band (VB) energy level alignment at perovskite/HTL interface. Furthermore, according to the equation $E_c = E_v - E_g$, the conduction-band energy levels ($E_c$) of the spiro-OMeTAD+CNT and spiro-OMeTAD+CNT:TiO$_2$ films are calculated to be about $-2.18$ and $-2.19$ eV, respectively. Therefore, for both doping spiro-OMeTAD films, the $E_c$ is slightly higher than that of the control spiro-OMeTAD ($-2.24$ eV) and much higher than that of the perovskite ($-3.93$ eV), as shown in Figure 1B. To further prove that the doping CNT:TiO$_2$ is more conducive to hole transfer than the CNT at the CH$_3$NH$_3$PbI$_3$/spiro-OMeTAD+CNT:TiO$_2$ interface, the surface potential distribution of the films with the CNT and CNT:TiO$_2$ additives under illumination are characterized by KPFM. Figure 3C and E show the surface morphology of the films with CNT and CNT:TiO$_2$, respectively. The corresponding potential distributions are shown in Figure 3D and F, respectively. Compared with the film with CNT, the film with CNT:TiO$_2$ has higher surface potential, which is obviously due to the more effective hole separation at CH$_3$NH$_3$PbI$_3$/spiro-OMeTAD+CNT:TiO$_2$ interface caused by the doping CNT:TiO$_2$.

To study the effects of CNT-doped spiro-OMeTAD layer (spiro-OMeTAD+CNT) and CNT:TiO$_2$-doped spiro-OMeTAD layer (spiro-OMeTAD+CNT:TiO$_2$) on the device performance, we first optimized the concentration of CNT and CNT:TiO$_2$ in spiro-OMeTAD HTL.
Figures 4A and B show the statistic distributions of PCEs for the PSCs based on spiro-OMeTAD+CNT and spiro-OMeTAD+CNT:TiO2 with different concentrations. PCE histograms of PSCs with different, C, CNT and, D CNT:TiO2 concentrations.

Table 1 Performance parameters of PSCs with different CNT concentrations

| CNT (mg mL⁻¹) | Voc (V) | Jsc (mA cm⁻²) | FF  | Best PCE (%) | Average PCE (%) |
|---------------|---------|---------------|-----|--------------|-----------------|
| 0             | 1.09 ± 0.02 | 21.67 ± 0.34  | 0.74 ± 0.01 | 17.90         | 17.30 ± 0.60    |
| 0.005         | 1.09 ± 0.01 | 22.72 ± 0.27  | 0.74 ± 0.01 | 19.09         | 18.31 ± 0.41    |
| 0.025         | 1.10 ± 0.01 | 22.96 ± 0.30  | 0.76 ± 0.01 | 19.82         | 19.27 ± 0.24    |
| 0.05          | 1.08 ± 0.02 | 22.82 ± 0.71  | 0.73 ± 0.01 | 19.19         | 17.92 ± 0.81    |
| 0.1           | 1.07 ± 0.01 | 21.20 ± 0.21  | 0.73 ± 0.01 | 17.11         | 16.63 ± 0.19    |

Table 2 Performance parameters of PSCs with different CNT:TiO2 concentrations

| CNT:TiO2 (mg mL⁻¹) | Voc (V) | Jsc (mA cm⁻²) | FF  | Best PCE (%) | Average PCE (%) |
|--------------------|---------|---------------|-----|--------------|-----------------|
| 0                  | 1.09 ± 0.02 | 21.67 ± 0.34  | 0.74 ± 0.01 | 17.90         | 17.30 ± 0.60    |
| 0.005              | 1.10 ± 0.01 | 23.12 ± 0.57  | 0.75 ± 0.01 | 19.81         | 19.01 ± 0.81    |
| 0.025              | 1.11 ± 0.01 | 24.24 ± 0.40  | 0.77 ± 0.01 | 21.53         | 20.72 ± 0.77    |
| 0.05               | 1.11 ± 0.01 | 23.00 ± 1.01  | 0.76 ± 0.01 | 20.75         | 19.40 ± 1.30    |
| 0.1                | 1.10 ± 0.01 | 21.45 ± 0.11  | 0.73 ± 0.02 | 17.78         | 17.23 ± 0.61    |

Figures 4A and B show the statistic distributions of PCEs for the PSCs based on spiro-OMeTAD+CNT and spiro-OMeTAD+CNT:TiO2 with different concentrations and the corresponding PCE histograms are shown in Figure 4C and D, respectively. The performance parameters for the PSCs with spiro-OMeTAD+CNT and spiro-OMeTAD+CNT:TiO2 HTLs have been listed in Tables 1 and 2. It can be found that, for both the CNT and CNT:TiO2, the optimum concentration is 0.025 mg mL⁻¹.

With the optimum concentration of the CNT and CNT:TiO2, we compared the performance of the champion devices based spiro-OMeTAD, spiro-OMeTAD+CNT, and spiro-OMeTAD+CNT:TiO2 HTLs. Figure 5A shows the J-V characteristics of PSCs based on pristine spiro-OMeTAD and doping spiro-OMeTAD HTLs under AM1.5G solar illumination (100 mW cm⁻²). The performance parameters of PSCs such as open circuit voltage (Voc), short-circuit current density (Jsc), and fill factor...
(FF) are listed in Table 3. The PSC with spiro-OMeTAD + CNT displays a $V_{oc}$ of 1.10 V, a $J_{sc}$ of 22.96 mA cm$^{-2}$, and a FF of 0.76, yielding a PCE of 19.82% at forward scans (FS) and 19.07% at reverse scan (RS), respectively. Compared with the PCE of 17.90% at FS and of 17.28% at RS of the PSC with pristine spiro-OMeTAD, the PCE of the PSC with spiro-OMeTAD+CNT is increased by more than 10%. After doping with TiO$_2$ NPs modified CNT (ie, CNT:TiO$_2$), the PCE of the cell was further increased to 21.53% ($V_{oc} = 1.11$ V, $J_{sc} = 24.24$ mA cm$^{-2}$, and FF = 0.77) at FS, which is increased by nearly 15% compared with that based on pristine spiro-OMeTAD. Figure 5B displays the IPCE spectra of as-prepared devices, which shows that the IPCE of the spiro-OMeTAD+CNT-based PSC is higher than that of the pristine spiro-OMeTAD-based cell and the IPCE is further improved by TiO$_2$-modified CNT. The integrated photocurrent values estimated from the IPCE spectra (20.10 mA cm$^{-2}$ for spiro-OMeTAD, 22.22 mA cm$^{-2}$ for spiro-OMeTAD+CNT, and 23.62 mA cm$^{-2}$ for spiro-OMeTAD+CNT:TiO$_2$, respectively) are consistent with the measured $J_{sc}$ values (Table 1). For the long-time stability test, uncapacitated PSCs stored in ambient environment (~50% relative humidity) at room temperature were tested in the light and the results are displayed in Figure 5C. The spiro-OMeTAD+CNT:TiO$_2$-based cells exhibited a loss in PCE of about 15% in 240 hours of monitoring, while the devices based on the spiro-OMeTAD and spiro-OMeTAD+CNT lost about 90% and 35% of their initial efficiency, respectively. Therefore, the cell based on spiro-OMeTAD+CNT:TiO$_2$ material shows the best stability, which is because the spiro-OMeTAD + CNT:TiO$_2$ layer has the best hydrophobic property and the least defect density of states compared with the spiro-OMeTAD and spiro-OMeTAD+CNT, thus effectively slowing down the water penetration into the perovskite layer in the atmospheric environment, and increasing the stability of the device (See Figure S3).Figure 5D shows

| Devices with different HTLs | Voc (V) | $J_{sc}$ (mA cm$^{-2}$) | FF | Best PCE (%) | Average PCE (%) |
|-----------------------------|--------|------------------------|----|--------------|-----------------|
| spiro-OMeTAD FS             | 1.09 ± 0.02 | 21.67 ± 0.34 | 0.74 ± 0.01 | 17.90 | 17.30 ± 0.60 |
| spiro-OMeTAD RS             | 1.08 ± 0.02 | 21.63 ± 0.21 | 0.68 ± 0.06 | 17.28 | 15.87 ± 1.10 |
| spiro-OMeTAD+CNT FS         | 1.10 ± 0.01 | 22.96 ± 0.30 | 0.76 ± 0.01 | 19.82 | 19.27 ± 0.24 |
| spiro-OMeTAD+CNT RS         | 1.09 ± 0.01 | 22.37 ± 0.45 | 0.75 ± 0.01 | 19.07 | 18.48 ± 0.22 |
| Spiro-OMeTAD+CNT:TiO$_2$ FS | 1.11 ± 0.01 | 24.24 ± 0.40 | 0.77 ± 0.01 | 21.53 | 20.72 ± 0.77 |
| spiro-OMeTAD+CNT:TiO$_2$ RS | 1.09 ± 0.01 | 24.18 ± 0.27 | 0.75 ± 0.02 | 20.70 | 19.70 ± 0.51 |

FIGURE 5 A, $J$-$V$ curves and, B, IPCE of the best devices of PSCs based on different HTLs, spiro-OMeTAD (black), Sprio-OMeTAD+CNT (blue), Sprio-OMeTAD+CNT:TiO$_2$ (red)
the statistical distributions of the performance parameters with 15 cells in each type of device. The spiro-OMeTAD-based solar cell yields an average PCE of 17.20%. With the incorporation of CNT and CNT:TiO₂ into the spiro-OMeTAD, the average PCE of the solar cell increases dramatically to 19.05% and 20.71%.
Furthermore, to eliminate the influence of Li-TFSI on the performance of PSCs, the \( J-V \) characteristics of PSCs based on HTLs without Li-TFSI under AM1.5G solar illumination (100 mW cm\(^{-2}\)) are also measured, as shown in Figure S4. The performance parameters are summarized in Table S1. Compared with the PSCs with Li-TFSI-incorporated HTLs, the PCEs of all three kinds of PSCs decreased obviously, which can be attributed to low hole conductivity of pristine spiro-OMeTAD layer. In spite of this, the incorporated CNT and CNT-TiO\(_2\) still significantly improve the PCE of the PSCs based on pristine Spiro-OMeTAD without Li-TFSI, which proves the effectiveness of CNT and CNT-TiO\(_2\) in improving the PCE of the PSCs.

To reveal the reason why incorporated CNT and CNT-TiO\(_2\) in spiro-OMeTAD HTL significantly improve the PCE and stability of PSCs, the \( J-V \) characteristics of PSCs based on HTLs without Li-TFSI under AM1.5G solar illumination (100 mW cm\(^{-2}\)) are also measured, as shown in Figure S4. The performance parameters are summarized in Table S1. Compared with the PSCs with Li-TFSI-incorporated HTLs, the PCEs of all three kinds of PSCs decreased obviously, which can be attributed to low hole conductivity of pristine spiro-OMeTAD layer. In spite of this, the incorporated CNT and CNT-TiO\(_2\) still significantly improve the PCE of the PSCs based on pristine Spiro-OMeTAD without Li-TFSI, which proves the effectiveness of CNT and CNT-TiO\(_2\) in improving the PCE of the PSCs.

To reveal the reason why incorporated CNT and CNT-TiO\(_2\) in spiro-OMeTAD HTL significantly improve the PCE and stability of PSCs, the \( J-V \) characteristics of spiro-OMeTAD+Cu and spiro-OMeTAD+Cu/TiO\(_2\) HTLs first studied because of the important influence of \( \sigma \) of HTL on the performance of PSCs.\(^{40}\) Figure 6A displays the \( J-V \) characteristics of three kinds of resistance devices that HTLs are sandwiched between FTO and Au (eg, FTO/spiro-OMeTAD/Au, FTO/spiro-OMeTAD+CNT/Au, and FTO/spiro-OMeTAD+CNT/TiO\(_2\)/Au). The \( \sigma \) can be obtained using the equation: \( \rho = L/R \times S \), where \( R \) is the resistance, \( L \) is the thickness of HTL, \( S \) is the public area between FTO and Au. 1/R\( \times \)S can be obtained from Figure 6A. Then the \( \sigma \) for spiro-OMeTAD is \( 5.83 \times 10^{-4} \) S cm\(^{-1}\), which is comparable to previous report.\(^{41}\) And the \( \sigma \) for spiro-OMeTAD+CNT and spiro-OMeTAD+CNT/TiO\(_2\) are 8.51 and \( 10.4 \times 10^{-4} \) S cm\(^{-1}\), which are much higher than that for spiro-OMeTAD. In particular, the conductivity of spiro-OMeTAD+CNT/TiO\(_2\) is 78% higher than that of pristine spiro-OMeTAD.

To reveal the intrinsic mechanism that TiO\(_2\) NPs enhance the conductivity of spiro-OMeTAD+CNT/TiO\(_2\) film, first principles method is used to calculate the density of states (DOSs) of CNT and CNT-TiO\(_2\) (Figure 6B,C). Compared with the CNT, the CNT-TiO\(_2\) has a significantly higher DOSs around the Fermi level, leading to a higher conductivity. Furthermore, the partial DOS (PDOS) of CNT/TiO\(_2\) is shown in Figure 6D, from which it can be seen that the increased DOSs of CNT/TiO\(_2\) mainly originate from strong interaction between C atoms of CNT and Ti atoms of TiO\(_2\) NPs as shown in the charge density difference map of CNT/TiO\(_2\) (inset of Figure 6D).

To investigate the influence of CNT and CNT-TiO\(_2\) on the kinetics of charge transfer at the perovskite/spiro-OMeTAD interface, the steady-state PL and TRPL decay of the CH\(_3\)NH\(_3\)PbI\(_3\)/HTL films are measured and shown in Figure S2. Figure S2a shows that all the samples show a strong PL peak around 770 nm, and the PL intensity of CH\(_3\)NH\(_3\)PbI\(_3\)/spiro-OMeTAD+CNT is significantly lower than that of CH\(_3\)NH\(_3\)PbI\(_3\)/spiro-OMeTAD. After the incorporation of the CNT/TiO\(_2\), the PL intensity of CH\(_3\)NH\(_3\)PbI\(_3\)/spiro-OMeTAD+CNT/TiO\(_2\) is further reduced, suggesting that the transfer of photo-generated holes is the most effective at the CH\(_3\)NH\(_3\)PbI\(_3\)/spiro-OMeTAD+CNT/TiO\(_2\) interface. The charge transfer process was quantitatively analyzed by TRPL at 770 nm (Figure S2b) and TRPL shows a similar result, that is, the CH\(_3\)NH\(_3\)PbI\(_3\)/spiro-OMeTAD+CNT/TiO\(_2\) film shows the shortest charge recombination lifetime \( \tau \) (43.3 ns) compared with the CH\(_3\)NH\(_3\)PbI\(_3\)/spiro-OMeTAD+CNT and CH\(_3\)NH\(_3\)PbI\(_3\)/spiro-OMeTAD films, indicating that the spiro-OMeTAD+CNT/TiO\(_2\) film has the most effective charge extraction at the CH\(_3\)NH\(_3\)PbI\(_3\)/spiro-OMeTAD+CNT/TiO\(_2\) interface, which is part of the reason why spiro-OMeTAD+CNT/TiO\(_2\)-based solar cell exhibits the highest photocurrent density. These results can be explained as follows. On the one hand, compared with the spiro-OMeTAD+CNT and spiro-OMeTAD+CNT:TiO\(_2\) HTLs, the spiro-OMeTAD film has the lowest hole mobility, so the charge transfer at the CH\(_3\)NH\(_3\)PbI\(_3\)/spiro-OMeTAD interface is the slowest, resulting in the strongest PL intensity and longest carrier lifetime. On the other hand, compared with the spiro-OMeTAD+CNT film, spiro-OMeTAD+CNT/TiO\(_2\) film has lower \( E_v \) and
the higher conductivity, which is more conducive to the hole transfer, resulting in that the film with spiro-OMeTAD+CNT:TiO$_2$ has the lowest PL intensity and the shortest carrier lifetime.

To understand the effects of incorporated CNT and CNT:TiO$_2$ on charge recombination kinetics and interfacial charge transfer in PSCs, the dependence of $J_{sc}$ and $V_{oc}$ on light intensity $I$ (50, 80, 100, 120, and 150 mW cm$^{-2}$, respectively), and Mott-Schottky (M-S) plots of PSCs with different HTLs are measured and the results are shown in Figure 7. There are mainly two kinds of charge recombination processes in PSCs, namely bimolecular recombination and trap-assisted recombinations, and the closer the slope is to 1 $kT/e$, the less the trap density is. Figure 7A shows the slopes of the devices with spiro-OMeTAD, spiro-OMeTAD+CNT and spiro-OMeTAD+CNT:TiO$_2$ are 1.15, 1.09, and 1.01 $kT/e$, respectively, which suggests that trap density are fewer at the CH$_3$NH$_3$PbI$_3$/spiro-OMeTAD+CNT interface, and fewest at the CH$_3$NH$_3$PbI$_3$/spiro-OMeTAD+CNT:TiO$_2$ interface. Figure 7B displays the measured $J(V)$ vary logarithmically with the $J(T)$. The slope (1.02) for the spiro-OMeTAD+CNT-based device is closer to 1 compared with that of the spiro-OMeTAD-based device (1.05), and the slope is 1.00 for the spiro-OMeTAD+CNT:TiO$_2$-based device, suggesting a less and least trap-assisted charge recombination for HTLs doping CNT and CNT:TiO$_2$. Furthermore, the space-charge-limited current (SCLC) measurements were used to obtain the defect state filling voltage $V_{TFL}$ (Figure 7C) and the density of defect states ($n_{trap}$) of the PSCs was estimated by equation $n_{trap} = 2e_{0}V_{TFL}/kT/L^{2}$, where $e$ is the elementary charge, $e_0$ is vacuum permittivity, $\varepsilon$ is the dielectric constant of CH$_3$NH$_3$PbI$_3$ ($\varepsilon = 32$) and $L$ is the thickness of the CH$_3$NH$_3$PbI$_3$. With the addition of CNT, the $V_{TFL}$ decreased from 0.27 to 0.19 V. Accordingly, the $n_{trap}$ decreased from $3.31 \times 10^{15} \text{ cm}^{-2}$ to $2.33 \times 10^{15} \text{ cm}^{-2}$. Furthermore, with the incorporation of CNT:TiO$_2$, the $n_{trap}$ was significantly reduced to $2.45 \times 10^{15} \text{ cm}^{-2}$ with a $V_{TFL}$ of 0.02 V. Therefore, both CNT and CNT:TiO$_2$ can passivate the defects of perovskite, but the passivation effect of CNT:TiO$_2$ is much better than CNT.

To investigate the passivation mechanism of CNT and CNT:TiO$_2$ on perovskite defects and stability enhancement, first principles calculations are performed to investigate the atomic scale interaction at the CH$_3$NH$_3$PbI$_3$/CNT and CH$_3$NH$_3$PbI$_3$/CNT:TiO$_2$ interfaces. Figure 8A, B show the interfacial bonding interaction at the CH$_3$NH$_3$PbI$_3$/CNT interface. It can be observed that the interactions between the CH$_3$NH$_3$PbI$_3$ and the CNT are mainly the Coulomb electrostatic attraction due to the electron redistribution. However, the electrostatic attraction between the CH$_3$NH$_3^+$ and I$^-$ ions in CH$_3$NH$_3$PbI$_3$ and the CNT can still reduce the loss of these ions to a certain extent, thereby passivating the defect states in CH$_3$NH$_3$PbI$_3$. In contrast, Figure 8C and D show that, for the CH$_3$NH$_3$PbI$_3$/CNT:TiO$_2$ interface, there is strong atomic bonding interaction between the I atoms of CH$_3$NH$_3$PbI$_3$ and the Ti atoms of CNT:TiO$_2$, forming I-Ti bonds. Meanwhile, the H atoms of CH$_3$NH$_3$PbI$_3$ form H...O hydrogen bonds with the O atoms of CNT:TiO$_2$. Therefore, these formed I-Ti bonds and H...O hydrogen bonds may passivate the defects of perovskite at the CH$_3$NH$_3$PbI$_3$/CNT:TiO$_2$ interface more effectively compared with the weak Coulomb electrostatic interaction between the CH$_3$NH$_3$PbI$_3$ and CNT, which not only significantly reduces the density of defect states of perovskite/spiro-OMeTAD+CNT:TiO$_2$ film, but also effectively improves the structural stability of CH$_3$NH$_3$PbI$_3$ crystals at the CH$_3$NH$_3$PbI$_3$/CNT:TiO$_2$ interface, thus effectively promoting the efficiency and stability of the PSCs based on spiro-OMeTAD+CNT:TiO$_2$ HTL. In addition, the contact angle of water on the HTLs were also measured to study the effects of CNT and CNT:TiO$_2$ on the hydrophobicity of spiro-OMeTAD film to the water. Figure S3 shows that the contact angle for the spiro-OMeTAD+CNT and spiro-OMeTAD+CNT:TiO$_2$ HTLs increased to 61.16° and 68.30°, respectively compared with that (21.33°) of the pristine spiro-OMeTAD film, which suggests that CNT:TiO$_2$-doped spiro-OMeTAD has the best hydrophobicity, enhancing the stability of PSCs. Therefore, the improvement of performance stability benefits from two aspects: passivation of defect states and improvement of hydrophobicity of HTL.

The effects of CNT and CNT:TiO$_2$ on the charge extraction at the CH$_3$NH$_3$PbI$_3$/HTL interface are studied by the capacitance-voltage (C-V) measurements. Generally, the interfacial charge density can be revealed by the C-V curves, which is inversely proportional to the straight line slope of the M-S relation. Figure S5 depicts the M-S plots of PSCs with different HTLs at 10 kHz. Obviously, the slopes ($K_2 = 20.87$, and $K_3 = 20.98$) of the device with spiro-OMeTAD+CNT and spiro-OMeTAD+CNT:TiO$_2$ HTLs increased to 61.16° and 68.30°, respectively compared with that (21.33°) of the pristine spiro-OMeTAD film, which suggests that CNT:TiO$_2$-doped spiro-OMeTAD has the best hydrophobicity, enhancing the stability of PSCs. Therefore, the improvement of performance stability benefits from two aspects: passivation of defect states and improvement of hydrophobicity of HTL.

The effects of the CNT and CNT:TiO$_2$ on the charge recombination of PSCs are investigated using EIS measurements, and the results are illustrated in Figure S6, and the inset is a reported equivalent circuit to fit the experimental data. $R_s$ is the series resistance, $R_{trans}$ and $C_{trans}$ are the transport resistance and transport chemical capacitance, which are displayed at the high-frequency arc relating to the charge transport from the cathode to the anodes. $R_{rec}$ and $C_{rec}$ are the charge recombination resistance and the chemical capacitance which are integrated the recombination process at low-frequency arc.
The parameters obtained by fitting the experimental Nyquist spectra are listed in Table S2. With the addition of CNT and CNT:TiO₂ into pristine spiro-OMeTAD film, the value of $R_{\text{trans}}$ decreases from 772.59 to 429.27 Ω, indicating that the transport resistance of charge decreases gradually, while the value of $R_{\text{rec}}$ increases from 1007.13 to 1741.69 Ω, indicating that the charge recombination decreases gradually.

3 | CONCLUSIONS

In summary, we have fabricated highly improved PSCs by incorporating CNT:TiO₂ into spiro-OMeTAD HTL. With the incorporation of CNT and CNT:TiO₂, on the one hand, the conductivity of the doped spiro-OMeTAD HTL increases gradually, and the conductivity of the spiro-OMeTAD+CNT:TiO₂ film is 1.78 times that of pristine spiro-OMeTAD. On the other hand, the hydrophobicity of the doped spiro-OMeTAD HTL becomes better and the spiro-OMeTAD+CNT:TiO₂ HTL shows the best hydrophobicity. Besides, the defect passivation of CNT:TiO₂ on perovskite is realized by formed I-Ti bonds and H…O hydrogen bonds. Due to the multiple functions of doping CNT:TiO₂, namely the high conductivity, good hydrophobicity and passivation effect of spiro-OMeTAD+CNT:TiO₂ film, the spiro-OMeTAD+CNT:TiO₂ based solar cell achieves the highest efficiency of 21.53%, which is 1.2 times that of spiro-OMeTAD based device. Meanwhile, compared with pristine spiro-OMeTAD and spiro-OMeTAD+CNT based PSCs, the spiro-OMeTAD+CNT:TiO₂ based devices also exhibits the best long-term stability in a high humidity atmosphere without encapsulation. After 240 hours of monitoring in ambient conditions, the PCE of the spiro-OMeTAD+CNT:TiO₂ based cell without encapsulation can still maintain over 85% of its initial PCE. Our research shows that it is an effective way to improve the performance of perovskite solar cells through functionalized carbon nanotubes as activities.

4 | EXPERIMENTAL SECTION

4.1 | Materials and chemicals

Lead iodide (PbI₂, 99.99%), methylammonium iodide (MAI, ≥99.5%), glacial acetic acid, spiro-OMeTAD, Li-TFSI, TiO₂ paste (Dyesol 18NR-T), and 4-tert-butylpyridine (TBP) were purchased in advance (Xi’an Polymer Light Technology Corp). N,N-dimethyleformamide (DMF, 99%) and dimethylsulfoxide (DMSO, 99%) were purchased from Sigma–Aldrich. Titanium butoxide (≥99.0%), acetaldehyde acetone (1 mL) were added dropwise to anhydrous ethanol solution (9 mL) under agitation, and then deionized water of 1 mL was added slowly. The mixture was further stirred for 24 hours to obtain the cp-TiO₂ precursors. The compact TiO₂ (cp-TiO₂) films are deposited by spin-coating the cp-TiO₂ precursor (6500 rpm, 30 seconds) on FTO glasses, followed by a heat treatment process to obtain FTO/cp-TiO₂ film (550°C, 0.5 hour). To prepare mesopore TiO₂ (mp-TiO₂) precursor, TiO₂ paste (Dyesol 18NR-T) was diluted with anhydrous ethanol (at 1:7 weight ratio) and stirred for 8 hours. The mp-TiO₂ films were deposited by spin-coating mp-TiO₂ precursor on prepared FTO/cp-TiO₂ films (2000 rpm, 30 seconds), after which an annealing process (550°C, 0.5 hour) is carried out.

4.2 | Preparation of cp-TiO₂ and mp-TiO₂ films

First, titanium butanol (1 mL), glacial acetic acid (1 mL), and acetaldehyde acetone (1 mL) were added dropwise to anhydrous ethanol solution (9 mL) under agitation, and then deionized water of 1 mL was added slowly. The mixture was further stirred for 24 hours to obtain the cp-TiO₂ precursors. The compact TiO₂ (cp-TiO₂) films are deposited by spin-coating the cp-TiO₂ precursor (6500 rpm, 30 seconds) on FTO glasses, followed by a heat treatment process to obtain FTO/cp-TiO₂ film (550°C, 0.5 hour). To prepare mesopore TiO₂ (mp-TiO₂) precursor, TiO₂ paste (Dyesol 18NR-T) was diluted with anhydrous ethanol (at 1:7 weight ratio) and stirred for 8 hours. The mp-TiO₂ films were deposited by spin-coating mp-TiO₂ precursor on prepared FTO/cp-TiO₂ films (2000 rpm, 30 seconds), after which an annealing process (550°C, 0.5 hour) is carried out.

4.3 | Preparation of CNT:TiO₂ composites

CNT:TiO₂ composite structures were synthesized by hydrothermal method. First, ~10 mg single-walled CNTs were dispersed in 100 mL absolute alcohol in a 200 mL beaker and sonicated for 60 minutes. The resulting solution is labeled A. Second, 2 mL of butyl titanate was measured with a pipette gun and dispersed in 50 mL absolute ethanol and sonicated for 30 minutes. The resulting solution was recorded as B. The solution B was added drop by drop to solution A and sonicated for 60 minutes. Thirdly, the A-B mixture was further centrifuged, and the precipitates were dispersed in 50 mL absolute ethanol and sonicated for 30 minutes. The resulting solution was recorded as B. The solution B was added drop by drop to solution A and sonicated for 60 minutes. Finally, the cleaned precipitates were freeze-dried to obtain CNT:TiO₂ composite powder.

4.4 | Preparation of spiro-OMeTAD chlorobenzene solution containing CNT and CNT:TiO₂

The spiro-OMeTAD solution was prepared by dissolving spiro-OMeTAD, TBP and Li-TFSI in chlorobenzene, as
described previously in our paper. After that, CNT powder was dispersed in chlorobenzene with different concentrations (≤0.1 mg mL⁻¹) and the mixture was sonicated for 20 minutes and then magnetically stirred for 1 hour to obtain spiro-OMeTAD chlorobenzene solution containing CNT. The spiro-OMeTAD solution containing CNT:TiO₂ powder was obtained by the same method as for the spiro-OMeTAD chlorobenzene solution containing CNT, except that the CNT powder was replaced by CNT:TiO₂ powder.

4.5 Fabrication of solar cells

First, the mixed solution of DMF and DMSO was prepared with the volume ratio of 1:9, and then PbI₂ (478 mg) and CH₃NH₃I (165 mg) were dissolved into that mixed solution (1 mL) to prepare CH₃NH₃PbI₃ precursor solution and then the precursor solution was spin-coated onto the FTO/cp-TiO₂/mp-TiO₂ films (4000 rpm, 30 seconds). After the first 10 seconds of spin coating, the chlorobenzene as anti-solvent was quickly dropped onto the mp-TiO₂ films. To evaporate the solvent and improve the crystallinity of CH₃NH₃PbI₃ crystals, the spin-coated films were further annealed at 100 °C for 10 minutes. To deposited spiro-OMeTAD+CNT and spiro-OMeTAD+CNT:TiO₂ HTLs, pre-prepared spiro-OMeTAD+CNT and spiro-OMeTAD+CNT:TiO₂ precursors were spin-coated onto the CH₃NH₃PbI₃ films (5000 rpm, 30 seconds), respectively. Finally, the gold electrode (80 nm) was deposited by vacuum thermal evaporation. The control PSCs without the CNT were also fabricated for comparison, which are prepared by the same process as for the devices with CNT, expect for using pure spiro-OMeTAD to replace the spiro-OMeTAD containing CNT and CNT:TiO₂. For all PSCs, effective area is 0.04 cm².

4.6 Characterization and measurements

The ultraviolet/visible (UV/vis) absorption spectra were obtained from a UV/vis spectrometer (Lambda 950 from Perkin-Elmer). Ultraviolet photoelectron spectroscopy (UPS) spectra were conducted by Kratos AXIS-ULTRA DLD-600 W equipped with a He I lamp (hν = 21.20 eV) with an applied bias of −5 V. A scanning electron microscope (SEM, thermo scientific, Verios G4 UC) under an accelerating voltage of 1 kV was used to characterize the film morphologies. A JEOL JEM-1400 plus transmission electron microscopy (TEM) operating at 120 kV was used to TEM measurements. For low-resolution and high-resolution TEM (HR-TEM) imaging, the samples were prepared by dropping a dilute chlorobenzene solution of CNT:TiO₂ onto a copper grid (400-mesh) TEM grid. A Bruker atomic force microscopy (AFM) (Multimode 8.0, Bruker Co) was used for the Kelvin probe force microscopy (KPFM) measurement. The photo-luminescence (PL) spectrum and transient fluorescence spectrum (TRPL) were measured using a Horiba Jobin Yvon spectrophotometer analysis, where samples were excited from the FTO side by an EPL 515-nm pulsed laser. For the TRPL measurements, the PL decay was probed at 775 nm after light excitation and the lifetime was obtained by fitting the TRPL data with a bi-exponential decay function: \( I(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) \). The current-voltage (J-V) characteristics of as-prepared PSCs were measured in the forward-scan direction (1.2 to −0.1 V) by a Keithley 2400 source meter with a scan rate of 0.02 V s⁻¹ under ambient conditions (65% relative humidity). The light intensity of 100 mW cm⁻² (AM1.5 simulated irradiation) was adjusted by a standard Si reference cell (Japanese Industrial Standards). The IPCE spectra were recorded using a solar cell quantum efficiency test system (Crown tech Qtest Station 500ADX). Electrochemical impedance spectra (EIS) and Mott-Schottky measurements of the PSCs were performed on an electrochemical workstation (CHI660E, China Chenhua Equipment Co.) in a measurement frequency range of 0.1 to 10⁵ Hz. Z-view software is used to fit the measured EIS data.

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CONFLICT OF INTEREST

The authors declare no conflict of interest. [Correction added on 10 June 2021, after first online publication: Conflict of Interest section has been added.]

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**SUPPORTING INFORMATION**

Additional supporting information may be found online in the Supporting Information section at the end of this article.

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