ABSTRACT: Tin oxide (SnO₂) has recently emerged as a promising electron transport layer for perovskite solar cells (PSCs) in light of the material's optical and electronic properties and its low-temperature processing. However, SnO₂ films are prone to surface defect formation, which results in energy loss in PSCs. We report that surface treatment using ammonium fluoride (NH₄F) leads to reduced surface defects and that it also induces chemical doping of the SnO₂ substrate simultaneously. The effects of NH₄F treatment on SnO₂ properties are revealed by surface chemical analysis, computational studies, and energy level investigations, and PSCs with the treatment achieve photovoltaic performance of 23.2% in light of higher voltage than in relevant controls.

Metal oxide semiconductors have contributed to the development of perovskite solar cells (PSCs) by providing selective contacts. In early research on PSCs, mesoporous titanium oxide (TiO₂) electron transport layers (ETLs) were used, but these required high-temperature processes over 450 °C. Research has recently shifted to tin oxide (SnO₂)-based electron transport layers because of their higher electron mobility, reduced optical losses because of higher transmittance, and smaller refractive index difference between transparent conductive oxides (TCOs) such as indium tin oxide (ITO) or fluorine-doped tin oxide (FTO) composed of SnOₓ as well as low-temperature processing. The record for the highest PSC photovoltaic performance is held by devices that use a SnO₂ ETL.

Despite the excellence of SnO₂, the SnO₂ layer does have a drawback: metal oxides contain surface hydroxyl groups, and these generate trap states near the valence band. It is important to reduce the defect sites on the SnO₂ surface because these cause nonradiative recombination at the SnO₂/perovskite interface. There is also room to improve the electron extraction from the perovskite by tuning the SnO₂ energy level via doping.

We report a bifunctional surface treatment that uses ammonium fluoride (NH₄F) to reduce defect sites and adjust the Fermi level of SnO₂ thin films. This concept was inspired by the preparation of fluorine-doped SnO₂ (FTO) by reaction with tin(IV) tetrahydroxide (Sn(OH)₄) and NH₄F. We theorized that an NH₄F surface treatment could eliminate hydroxyl groups from the SnO₂ surface and also dope it with fluorine ions (Figure 1a). In agreement with previous literature, we determined that two kinds of hydroxyl groups exist on metal oxide surface: terminal-hydroxyls (OH⁻), which bind to one metal site with a basic characteristic, and bridge-hydroxyls (O−), which bind to two metal sites with an acidic characteristic. We expected that an ammonium cation with weak acidity from NH₄F would react with the OHT on the SnO₂ surface, forming ammonia gas and water vapor, and fluoride anions would substitute into the defect sites leading to tuning of the energy level.

We tested this idea by analyzing X-ray photoelectron spectroscopy (XPS) data for a pristine SnO₂ surface versus an NH₄F-treated SnO₂ surface (Figure 1b,c). The XPS spectra of O 1s for both samples (left column) show two distinct peaks for different oxygen species. A peak at 532.2 eV indicates the presence of a hydroxyl (−OH) group on the SnO₂ surface, and another peak at 530.3 eV originates from the saturated oxygen in SnO₂. By comparing the XPS spectra of O 1s, one sees that the ratio of hydroxyl group peak to saturated oxide peak is reduced from IHO/IO₂ = 1.85 (control) to 0.78 (NH₄F).

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In the Sn 3d XPS spectra of each sample (middle column), the peaks show an 8.4 eV difference, consistent with the tetravalent oxidation state of tin in SnO$_2$. The two peaks for the NH$_4$F-treated SnO$_2$ are downshifted 0.2 eV toward a lower binding energy compared to pristine SnO$_2$. In terms of fluorine (right column), the XPS spectrum of the NH$_4$F-treated SnO$_2$ shows doublet peaks, while that for pristine SnO$_2$ exhibits no signal. The fluorine signal indicates that NH$_4$F treatment induces fluorination on SnO$_2$ accompanying chemical doping. From XPS results of Sn 3d and F 1s for both samples, we conclude that the NH$_4$F treatment leads to the incorporation of fluorine on the SnO$_2$ surface.

We employed density functional theory (DFT) to explore the effects of the NH$_4$F treatment on the electronic properties of the SnO$_2$ surface. We chose the stoichiometric (110) surface for the study as it is the most thermodynamically stable configuration. This is in line with XPS spectra, which indicate that Sn is in the 4$^+$ state (Figure 1b), rather than the reduced 2$^+$ state which is typically found in a non-stoichiometric, oxygen-deficient surface. There are two main active sites on the surface; one is the bridge oxygen, and the other is the 5-fold-coordinated Sn (Figure 2a). The surface chemistry is determined by these dangling bonds, because they readily interact with water to form hydroxyl...
The under-coordinated metal atoms serve as Lewis acid attracting water molecules, and these dissociate and form two types of hydroxyl groups (Figure 2b) by transferring a proton to the nearby oxide ion. The XPS spectrum confirms the presence of an $\text{−OH}$ peak and the absence of an $\text{H}_2\text{O}$ peak (Figure 1b).

Figure 2a shows the band structure and the partial density of states (PDOS) of the stoichiometric (110) SnO$_2$ surface. The shaded area is the contribution from the bulk SnO$_2$ valence band maximum (VBM), and it serves as an energy reference across the different surface configurations. We note that the OH$_T$ in the hydroxylated surface introduces deep energy states in the bandgap (Figure 2b), which are traps that produce nonradiative recombination and result in energy loss.

We consider the following four cases when the hydroxylated surface is treated using NH$_4$F. The first and the most prominent reaction is between the ammonium cation and the OH$_T$ group, because OH$_T$ is basic and tends to dissociate as an $\text{−OH}$ anion. XPS shows that the concentration of hydroxyl groups is reduced by 58% after NH$_4$F treatment (Figure 1c). It is reasonable that most of the removed hydroxyl groups are OH$_T$ because of its basic nature and readiness to react with NH$_4^+$, while doubly bonded OH$_B$ is harder to remove. DFT predicts that the removal of terminal hydroxyl
groups eliminates trap states and thus can potentially improve the open-circuit voltage ($V_{OC}$) of a PSC (Figure 2c). In a second probable reaction with a terminal hydroxyl group, it is replaced with a fluorine atom through anion exchange, forming a terminal fluorine ($F_T$). The XPS spectrum of treated SnO$_2$ shows both a substitutional fluorine peak and another fluorine peak with a higher electron binding energy (Figure 1c). It is likely to be $F_T$, as the singly bonded fluorine accepts a reduced proportion of the electron density from Sn compared to the doubly bonded substitutional fluorine. Therefore, $F_T$ creates a more positive electrostatic potential to bind more strongly with the electron. DFT also predicts the removal of $OH_T$ trap states upon fluorine exchange (Figure S1b). The third scenario is the substitution of the bridge oxygen by fluorine, which is predicted to have a minimal effect on the band structure as it does not introduce trap states (Figure S1c). In the last case, where the fluorine bonds to a bridge oxygen, the electronic structure of the SnO$_2$ is significantly affected in terms of n-type doping (Figure 2d). Fluorine directly contributes to the shallow states below the conduction band minimum (CBM).

We investigated charge-transfer properties to study the effects of NH$_4$F treatment at the perovskite/SnO$_2$ interface. We did so by conducting a suite of photoluminescence (PL) spectroscopy measurements. The steady-state PL spectra (Figure 3a) show a higher quenching efficiency of 84% for NH$_4$F-treated samples, while pristine SnO$_2$ has a quenching efficiency of 77%, indicating that NH$_4$F treatment modifies the SnO$_2$ surface to favor electron extraction from the perovskite film. Figure 3b shows the time-resolved PL decay curves for the corresponding samples. The curves were fit using a
bien exponential decay function, yielding a fast decay ($\tau_1$) and a slow decay ($\tau_2$) component. The commonly accepted photoelectrical interpretation for perovskite/charge selective layer interfaces is that $\tau_1$ originates from the quenching of charge carriers by the charge selective layers, and $\tau_2$ is attributed to radiative recombination of free charge carriers in perovskite bulk.\textsuperscript{16}\textsuperscript{19} The lifetimes of the NH$_4$F-treated sample were calculated as having $\tau_1$ of 20 ns and $\tau_2$ of 143 ns, while the control sample showed a larger $\tau_1$ of 30 ns and a comparable $\tau_2$ of 146 ns, indicating that the NH$_4$F treatment leads to dynamically faster electron extraction.

Ultraviolet photoelectron spectroscopy (UPS) measurements were performed to estimate the work function ($W_F$) shift after NH$_4$F treatment on SnO$_2$. Figure 3c shows that the photoemission cutoff for NH$_4$F-treated SnO$_2$ is 16.98 eV, corresponding to a $W_F$ of 4.24 eV, while pristine SnO$_2$ has a $W_F$ of 4.48 eV. The NH$_4$F treatment upshifts the Fermi energy level of SnO$_2$ by 0.24 eV, a finding we attribute to fluorine doping of SnO$_2$.\textsuperscript{20} The $W_F$ shift via NH$_4$F treatment is consistent with the DFT calculation results that fluorine substitution on the SnO$_2$ surface generates doping energy levels near the conduction band minimum of SnO$_2$. The reduced $W_F$ from the NH$_4$F treatment indicates that the Fermi energy level of SnO$_2$ shifts further from that of the perovskite, enabling the built-in-potential for the photocatalytic device. We evaluated current–voltage plots of ITO/SnO$_2$/perovskite/Au to understand the effect of NH$_4$F treatment on resistance on SnO$_2$ (Figure S2). Resistances obtained from the slope of the plots indicate NH$_4$F treatment barely influences the charge transport properties of SnO$_2$.

To explore the impact of NH$_4$F-treated SnO$_2$ on photocatalytic performance, we fabricated devices on a TCO (ITO or FTO)/SnO$_2$/(FAPbI$_3$)$_{0.95}$(MAPbBr$_3$)$_{0.05}$/spirop-MeTAD/Au configuration, a planar n-i-p structure, and characterized performance (Figure 3d). We employed two kinds of SnO$_2$ substrates: spin-coating of a commercial SnO$_2$ nanoparticle dispersion on an ITO substrate and vertically dipping an FTO substrate in tin chloride solution, known as chemical bath deposition (CBD).\textsuperscript{21} When we used the nanoparticle (NP)-based ETL, devices with NH$_4$F-treated SnO$_2$ showed an improved power conversion efficiency (PCE) compared to that of control devices. Regarding devices made using CBD, devices with NH$_4$F-treated SnO$_2$ also achieved an improved PCE of 23.2% with a short-circuit current density ($J_{sc}$) of 24.6 mA/cm$^2$, a $V_{OC}$ of 1.16 V, and a fill factor (FF) of 81.4%, while the control device showed 22.4% with a $V_{OC}$ of 1.12 V. These results were evaluated for statistical significance by comparing the PCE and $V_{OC}$ data from the 12 devices (Figure S3). As comparing to NP-based and CBD-based devices, CBD-based devices showed higher performance regardless of NH$_4$F treatment. It might result from the roughness difference between both as discussed in previous literature.\textsuperscript{22} SnO$_2$ prepared by CBD on FTO substrate may have higher contact with perovskite film to allow more efficient electron extraction compared to SnO$_2$ prepared by spinning NP on the ITO substrate. The $V_{OC}$ improvement upon NH$_4$F treatment is attributed to healing of defects and fluorine doping on the SnO$_2$ surface, because energy loss at the perovskite/charge selective layer interface is caused by surface defects and energy level alignment.\textsuperscript{23} We measured current density–voltage curves along both bias scanning directions and also stabilized PCEs at the maximum power point. CBD-based devices treated with NH$_4$F showed negligible current hysteresis and enhanced stabilized PCE (Figures S4 and S5). We offer that NH$_4$F treatment on SnO$_2$ in PSCs leads to the enhanced $V_{OC}$ by reducing energy loss at the SnO$_2$/perovskite interface.

The bifunctional surface engineering strategy on SnO$_2$ using NH$_4$F heals surface defects and favorably tunes the Fermi energy level of SnO$_2$, as seen in XPS, UPS, and DFT calculations. PL measurements show this strategy renders SnO$_2$ substrates more efficient in electron transfer from the perovskite film. The surface modification leads to reduced energy losses in PSCs, resulting in improved efficiency.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsenergylett.0c01566.

Materials, device fabrication and characterization, and Figures S1–S5 (PDF)

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Notes

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