Ultraviolet Photocatalytic Degradation of Perovskite Solar Cells: Progress, Challenges, and Strategies

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The certified efficiency of perovskite solar cells (PSCs) has reached 25.5% within just around 10 years, approaching the highest reported value of mainstream silicon solar cells. The application of metal–oxide (MO) electron transport layers (ETLs), including TiO_2 and SnO_2, is crucial for achieving highly efficient PSCs because of their wonderful photoelectrical properties, resulting in n–i–p conventional structure devices, constantly breaking the world record efficiency. However, these MOETLs inevitably lead to the degradation of PSCs due to their photocatalytic activity under actual sunlight which includes ultraviolet (UV) range. Overcoming the UV photocatalytic degradation is still a great challenge for the state-of-the-art PSCs toward practical applications. Herein, the recent progress related to the UV photocatalytic degradation of PSCs induced by the MOETLs based on recent literature reports is reviewed, including the photocatalysis origin, degradation mechanism, challenges, and various strategies. Perspectives for future efforts in overcoming UV photocatalytic degradation are provided. It is believed that this review is advantageous for achieving stable PSCs under actual outdoor sunlight.

1. Introduction

Perovskite solar cells (PSCs) have received great attention due to their ever-increasing power conversion efficiency (PCE), low-cost materials, and easy solution preparation. The certified efficiency of PSCs reached 25.5%\(^1\) based on a lab scale, exceeding the performance of copper indium gallium selenide (CIGS) and CdTe thin-film solar cells and approaching the highest reported value of the mainstream silicon solar cell.\(^2\) The highest-efficiency devices generally use the regular n–i–p structure composed of a perovskite absorber between a metal oxide electron transport layer (MOETL) and an organic hole transport layer (HTL).\(^3\,^4\)

Miyasaka et al. first adopted CH\(_3\)NH\(_3\)PbI\(_3\) and CH\(_3\)NH\(_3\)PbBr\(_3\) as light absorbers in liquid electrolyte-based dye-sensitized solar cells using a thick TiO\(_2\) layer (=10 \(\mu\)m) as an electron collector. The first PSCs achieved a PCE of 3.8%.\(^5\) After that, tremendous efforts have been made for the PSCs based on TiO\(_2\). The PSCs included an n-type TiO\(_2\) ETL, a perovskite absorber layer, a p-type 2,2’,7,7’-tetrakis-(N,N-di-4-methoxyphenylamino)-9,9’-spirobifluorene (Spiro-OMeTAD) HTL, which has been the most typical and successful structure. Grätzel et al. achieved the first certified efficiency of 14.14% based on the aforementioned n–i–p structure with compact TiO\(_2\) (c-TiO\(_2\))/mesoporous TiO\(_2\) (m-TiO\(_2\)).\(^6\) In the following years, the performance of the PSCs based on TiO\(_2\) achieved tremendous progress. To remove the organic material in TiO\(_2\) paste and achieve high-quality m-TiO\(_2\) layer, a high-temperature sintering process (>500 °C) was generally needed.\(^6\)

To avoid high-temperature processing, low-temperature processed SnO\(_2\) was developed. Tian and co-workers adopted SnO\(_2\) thin films attained by spin coating SnO\(_2\) nanoparticles on indium-doped tin oxide (ITO) followed by low-temperature annealing at 200 °C, and a 13% PCE was achieved.\(^7\) Huge progress of SnO\(_2\)-based PSCs was reported by Fang and co-workers. They adopted thermal decomposition of SnCl\(_2\)-H\(_2\)O precursor at 180 °C in ambient air to form SnO\(_2\) film and achieved 17.21% efficiency.\(^8\) Later on, Hagfeldt et al. used low-temperature chemical bath deposition to grow SnO\(_2\) ETL and obtained almost hysteresis-free PCEs of 20.8%.\(^9\) In 2019, the PCE of the planar SnO\(_2\) PSCs reached a certified efficiency of 23.32%, which first surpassed that of m-TiO\(_2\) PSCs.\(^10\) Therefore, SnO\(_2\) has increasingly attracted great attention as an ETL for PSCs, and it is considered as the most promising alternative to TiO\(_2\). Up to date, all the world records of the certified PCE were achieved based on TiO\(_2\) or SnO\(_2\) n–i–p conventional structures since the PSCs appeared in 2009 (Figure 1).\(^1\,^3,^5,^6,^9,^10–15\) Recently, a PCE of 25.8% (certified 25.5%) has been achieved based on Cl-bonded SnO\(_2\).\(^11\) Thus, the important key to achieve state-of-the-art PSCs is the application of TiO\(_2\) or SnO\(_2\), due to its excellent electrical properties.
However, it is known that the excellent photoelectric properties of TiO$_2$ and SnO$_2$ make them to be “golden” photocatalysts simultaneously. In recent decades, TiO$_2$ and SnO$_2$ photocatalysis have been widely studied in various areas, such as water splitting and pollutant degradation.$^{[16-19]}$ When TiO$_2$ and SnO$_2$ are exposed to near-ultraviolet (UV) light, it will inevitably decompose the adjacent perovskite absorption layer and thus decrease the stability of PSCs.$^{[19,20]}$ In the International Electrotechnical Commission (IEC) standards on terrestrial photovoltaic (PV) modules, light stability requirements include 1) UV preconditioning test: the module should be exposed to high-intensity and continuous UV irradiation with a total exposure of $15 \text{kWh m}^{-2}$ and 2) light soaking: the module is to be irradiated with a total of $86 \text{kWh m}^{-2}$ of continuous standard outdoor sunlight (including UV).$^{[21-23]}$ Such instability cannot be avoided during device operation, even if they are well encapsulated. It is worthy to note that most of the reported top-level photostabilities of PSCs are always carried out by completely eliminating the UV light using a UV filter or adopting a white light-emitting diode (LED) without UV range.$^{[24,25]}$ It illustrates the importance of suppressing the photocatalytic activity of TiO$_2$ and SnO$_2$ for stable operation of PSCs.

In this review, we will focus on the recent progress related with the UV photocatalytic degradation of PSCs, including degradation mechanism, challenges, and strategies. First, we briefly summarize the recent progress and trends of the state-of-the-art PSCs and emphasize the importance of overcoming the UV photocatalytic degradation. Next, we review the degradation mechanism of perovskites under the UV photocatalytic effect of TiO$_2$ and SnO$_2$. Then, we provide a comprehensive summary of the recent efforts of improving the PSC stability against the UV photocatalytic effect through interface engineering, removing the UV, using ETLs with inferior or no photocatalytic activity, etc. Finally, after assessing these methods, we provide our perspective and views of strategies that suppress and even eliminate the UV photocatalytic degradation effect in efficient PSCs. We hope that this review will be advantageous to improve the operational stability of efficient n–i–p PSCs under outdoor natural light soaking without cutting the UV light.

2. The Properties of TiO$_2$ and SnO$_2$ as ETLs in PSCs

As mentioned earlier, the wonderful photoelectrical properties of TiO$_2$ and SnO$_2$ are crucial to achieving high efficiency in n–i–p conventional structure PSCs; however, their UV photocatalytic activity largely harms device operational stability.

2.1. Excellent Photoelectric Properties

As ideal electron transport materials for PSCs, they need to meet some requirements: 1) well-matched energy alignment to trigger electron transfer while blocking holes; 2) high transparency to allow efficient light harvesting; 3) excellent electron mobility to minimize charge accumulation; and 4) easy access to starting

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**Figure 1.** Evolution in PSCs using TiO$_2$ or SnO$_2$ as ETL. The blue champion flags$^{[4,7-9]}$ and red champion flags$^{[1,3,5,6,10-15]}$ show the important milestones and the certified PSCs’ performance given in NREL.
materials with high chemical resistance to perovskite solvents (Figure 2a).\cite{26,27} TiO\textsubscript{2} and SnO\textsubscript{2} seem to be almost perfect ETLs for application in PSCs as they meet the earlier characteristics well.\cite{28,29}

### 2.1.1. Band Structure

TiO\textsubscript{2} mainly occurs in nature as the following well-known minerals, rutile, anatase, and brookite, which have different characteristics of Ti—O bonds.\cite{30} Among these three phases, the anatase phase has a wider bandgap of 3.2–3.5 eV and it is the most common one in PSCs. The bandgaps of SnO\textsubscript{2} reported range from 3.5 to 4.0 eV, depending on its specific synthesis conditions. The suitable conduction band (CB) of TiO\textsubscript{2} and SnO\textsubscript{2} (3.8–4.3 eV) contributes to the effective electron extraction from perovskite and the deep valence band (VB) around 7.2–7.9 eV can effectively prevent the hole from reaching the transparent electrodes.\cite{31,32} With a wide bandgap, they are advantageous in maximizing the light absorption of the perovskite layer by allowing more light to pass through them. The good band alignment of TiO\textsubscript{2} or SnO\textsubscript{2} with the perovskite layer theoretically ensures a high quality of the p–n heterojunction, which implies improved electric parameters.

### 2.1.2. Optical and Electrical Properties

TiO\textsubscript{2} and SnO\textsubscript{2} have superior light transmittance due to the wide bandgap and small reflective index of 2.4–2.5 and <2, respectively.\cite{33} The efficient light management in the UV-visible region offers a photon which can pass through easily and be absorbed by the perovskite absorber. The electron mobility of bulk TiO\textsubscript{2} is about <1 cm\textsuperscript{2} V\textsuperscript{-1} s\textsuperscript{-1}, and there are many effective ways to enhance the electron transfer capability, such as metal doping.\cite{34,35} In case of SnO\textsubscript{2}, it has high electron mobility (up to 421 cm\textsuperscript{2} V\textsuperscript{-1} s\textsuperscript{-1}) and high conductivity (≈1.7 S cm\textsuperscript{-1} for crystalline and ≈7.2 × 10\textsuperscript{-8} S cm\textsuperscript{-1} for amorphous SnO\textsubscript{2}), suggesting high electron collection efficiency and transport ability.\cite{36}

### 2.1.3. Chemical Stability and Easy Preparation

The TiO\textsubscript{2} and SnO\textsubscript{2} materials have excellent chemical stability. The lower hygroscopicity and acidity resistance contribute to the durability of the PSC device, which enables compatibility with various fabrication methods.\cite{37} The exploited techniques for the preparation of TiO\textsubscript{2} and SnO\textsubscript{2} have been reported with several different methods, mainly including the sol–gel method, nanocrystal approach, chemical bath deposition, the atomic layer deposition technique, electrodeposition, and so on.\cite{32,33}

### 2.2. Photocatalytic Activities of SnO\textsubscript{2} and TiO\textsubscript{2}

As the bandgap of TiO\textsubscript{2} and SnO\textsubscript{2} (3.2–3.8 eV) corresponds to 410 and 326 nm, the excitation wavelength almost falls in the UV region. Given that ≈3–5% of UV radiation in total solar flux is incident at the Earth’s surface,\cite{38,39} the excitation of MO by photons with light energy greater than the bandgap will generate holes and electrons, leading to interfacial redox reactions named the photocatalytic reaction (Figure 2b).\cite{18,40} For MO photocatalysis, the generation of the electron–hole pair can be written as follows:

\[
\text{MO} + \text{hv} \rightarrow \text{e}^- (\text{MO}) + \text{h}^+ (\text{MO})
\]

Electrons in the filled VB will be excited to the vacant CB, leaving holes in the VB. After electron–hole pair separation, the electrons or holes that migrate to the surface will drive the reduction or oxidation reactions, respectively. Therefore, a whole photocatalytic reaction can be broken down into the following two half reactions: an electron-induced reduction reaction and a hole-induced oxidation reaction. Photocatalytic reactions generally occur at the MO surface. It means that the photocatalytic process will inevitably occur in PSCs during their operation under natural solar light. However, the characterization of these fundamental processes is very complicated.

### 3. Photocatalytic Degradation Mechanism of PSCs

Although the UV photocatalytic degradation of PSCs is widely mentioned in numerous reports, studies related to the mechanism for the degradation reaction of perovskite are still rare.

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**Figure 2.** a) The typical n–i–p device structure and the requirements of ETL and b) the schematic processes in MO photocatalysis. Reproduced with permission.\cite{40} Copyright 1995, American Chemical Society.
3.1. Photocatalytic Degradation of PSCs Induced by TiO2

Snaith and co-workers first investigated the UV aging effect on the stability of m-TiO2 PSCs.[41] The PSCs were exposed to the simulated AM 1.5 sunlight. They found that when a UV filter was used, the PSCs were more stable. However, the encapsulated device was unstable when exposed to unfiltered simulated sunlight. They studied the surface chemistry of TiO2 and proposed the mechanism responsible for photocurrent degradation in the solar cells. Upon UV light exposure, an electron–hole pair will be formed after the excitation of TiO2 by UV light with energy higher than the bandgap of TiO2. Then photogenerated holes in m-TiO2 react with oxygen absorbed at surface oxygen vacancies, which then become deep traps leading to charge recombination. As TiO2 has a strong ability to extract electrons from organic materials as photocatalysts and from iodide anion (I\textsuperscript{-}) as electrodes in dye-sensitized solar cells, the driving force of decomposition was thought to result from the effect of electron extraction by TiO\textsubscript{2} from I\textsuperscript{-}.

Ito et al. showed the degradation scheme of CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3} PSCs resulting from TiO\textsubscript{2} during light exposure in Figure 3a, and the relevant equations are as follows.

\[
\text{CH}_3\text{NH}_3\text{PbI}_3 \rightleftharpoons \text{PbI}_2 + \text{CH}_3\text{NH}_2 \uparrow + \text{HI} \uparrow \tag{1}
\]

\[
2\text{I}^- \rightleftharpoons \text{I}_2 + 2\text{e}^- \tag{2}
\]

\[
3\text{CH}_3\text{NH}_3^+ \rightleftharpoons 3\text{CH}_3\text{NH}_2 \uparrow + 3\text{H}^+ \tag{3}
\]

\[
\text{I}^- + \text{I}_2 + 3\text{H}^+ + 2\text{e}^- \rightleftharpoons 3\text{HI} \uparrow \tag{4}
\]

It speculated that TiO\textsubscript{2} can extract electrons from I\textsuperscript{-}, resulting in the I\textsubscript{2} product at the surface of TiO\textsubscript{2} (Equation (2)), which deconstructs the perovskite crystal (Equation (3)). Then, the extracted electron that returned from the TiO\textsubscript{2} surface reacted with H\textsuperscript{+}, which resulted into further decomposition of the perovskite (Equation (4)).[42]

Similarly, Wang and co-workers deemed that the emergence of I\textsubscript{2} under UV light soaking is the main reason affecting stability.[43] The related equations have shown that the electrons in the CB of TiO\textsubscript{2} could induce the oxygen adsorbed on the vacancies of TiO\textsubscript{2} into hydroxyl radicals and H\textsubscript{2}O under UV light soaking, leading to a loss of CH\textsubscript{3}NH\textsubscript{3}\textsuperscript{+}, as shown in Equation (7) and (8). Meanwhile, both hydroxyl radicals and holes could oxidize I\textsuperscript{-} into I\textsubscript{2}, as shown in Equation (9) and (10).

\[
\text{TiO}_2 \xleftarrow{\text{hv}} e^-_{\text{CB}} + h^+_{\text{VB}} \tag{5}
\]

\[
h^+_{\text{VB}} + \text{I}^- \rightarrow \text{I} \cdot \tag{6}
\]

\[
\text{CH}_3\text{NH}_3^+ + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{NH}_2 + \text{H}_3\text{O}^+ \tag{7}
\]

\[
3e^-_{\text{CB}} + \text{O}_2 + 3\text{H}^+ \rightarrow \text{H}_2\text{O} + \text{OH} \cdot \tag{8}
\]

\[
\text{I}^- + \text{OH} \cdot \rightarrow \text{I} \cdot + \text{OH}^- \tag{9}
\]

\[
2\text{I} \cdot \rightarrow \text{I}_2 \tag{10}
\]

Li and co-workers proposed a two-stage degradation process (Figure 3b) of TiO\textsubscript{2}-based PSCs under continuous UV irradiation in an inert atmosphere.[44] After excitation by UV light, the VB electrons of TiO\textsubscript{2} transit to the CB, leaving free holes (step 1).

![Figure 3. Proposed mechanism for UV-induced perovskite degradation by: a) Ito et al., Reproduced with permission. Copyright 2014, American Chemical Society. b) Li et al., Reproduced with permission. Copyright 2020, Elsevier. c) Photographs of the mixtures of perovskite single-crystal powder and SnO\textsubscript{2} nanoparticle under UV illumination and d) the schematic diagram of the decomposition of Pb\textsubscript{X} under photocatalysis. Reproduced with permission.](https://www.advancedsciencenews.com)

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Unpaired electrons at the Ti$^{3+}$–VO site tend to recombine the holes in the VB (step 2). The Ti$^{4+}$–VO states capture photogenerated electrons from the perovskite layer (step 3), reverting Ti$^{4+}$–VO to Ti$^{3+}$–VO. The accumulation of photoelectrons provides extra electron recombination channels to holes in the perovskite layer (step 5) and/or HTL layer (step 6), leading to performance degradation of PSCs. With UV irradiation continuing, the concentration of Ti$^{4+}$–VO defect states increases, resulting from the reaction equilibrium of defects transformation and the increase in Ti$^{3+}$–VO, leading to the continuous degradation of device performance. The decomposition process of perovskite materials under UV irradiation can be described by the following four chemical equations.

\[ \text{Ti}^{4+} \xrightarrow{h^+} \text{Ti}^{3+} + e^- \quad (11) \]

\[ 2\text{Ti}^{4+} + \text{Pb}_2\text{I}_6^2- \xrightarrow{h^+} 2\text{Ti}^{3+} + 2\text{PbI}_2 + \text{I}_2 \quad (12) \]

\[ \text{I}_2 + \Gamma^- = \text{I}_3^- \quad (13) \]

\[ 3\text{CH}_3\text{NH}_3^+ + \text{I}_3^- + 2e^- \rightarrow 3\text{CH}_3\text{NH}_2^- + 3\text{HI} \quad (14) \]

First, oxygen vacancy–Ti$^{3+}$ (Ti$^{3+}$–VO) transforms into active Ti$^{3+}$–VO trap states under UV excitation and causes photocarrier loss (Equation (11)). Secondly, Ti$^{3+}$–VO states can convert back into Ti$^{4+}$–VO states (Equation (12)), through oxidizing \( \Gamma^- \), which result in the accumulation of \( \text{I}_3^- \) (Equation (13)). Sequentially, the rapid decomposition of perovskite accelerated by increasing \( \text{I}_3^- \) replaces the photocarrier loss as the dominant mechanism, leading to the second decay stage (Equation (14)).

### 3.2. Photocatalytic Degradation of PSCs Induced by SnO$2$

Although SnO$2$ is considered as an ETL with inferior photocatalytic activity compared with TiO$2$, it is also a cause for serious destruction of the perovskite under UV illumination. Hang et al. investigated the UV photocatalysis degradation of perovskite induced by SnO$2$.[45] They uniformly mixed three types of perovskite single-crystal powders (MAPbI$_3$, MAPbBr$_3$, and MAPbCl$_3$) with SnO$_2$ nanoparticles and exposed them to continuous UV illumination for several days (Figure 3c). The degrees of perovskite degradation under UV can be observed from the color of the powders. The X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) measurements were carried out to precisely elucidate the effect of photocatalysis for the stability of MAPbI$_3$, MAPbBr$_3$, and MAPbCl$_3$ perovskites. It was observed that PbX$_2$ (X = I, Br, Cl) and Pb$^0$ product in the MAPbI$_3$:SnO$_2$ case increased much faster than those in MAPbBr$_3$:SnO$_2$ and MAPbCl$_3$:SnO$_2$ cases.

Based on the earlier results, they proposed that the degradation procedure of MAPbI$_3$ under SnO$_2$ photocatalysis is expressed as the following.

\[ \text{CH}_3\text{NH}_3\text{PbI}_3 \rightarrow \text{CH}_3\text{NH}_2\text{I} + \text{PbI}_2 \quad (15) \]

\[ \text{PbI}_2 \rightarrow \text{Pb}^0 + \text{I}_2 \quad (16) \]

In the first stage of degradation (Equation (15)), the perovskite decomposed and PbI$_2$ product generated. Then, the PbI$_2$ can be further decomposed into Pb$^0$ and I$_2$ (Equation (16)) through interfacial redox reactions of electron–hole pairs, which are generated upon bandgap excitation when SnO$_2$ is exposed to UV light (Figure 3d). It is known that both Pb$^0$ and I$_2$ severely degrade the performance of PSCs as well as their long-term photostability. In addition, they demonstrated that the chlorine-based perovskite possesses the best tolerance for photocatalysis compared with the bromine-based and iodine-based perovskite owing to the strong Pb—Cl bond.

### 4. Strategies

The photocatalytic degradation of PSCs needs two basic factors: UV light and ETLS with photocatalytic activity. Thus, various types of strategies were proposed: 1) removing the UV spectrum through using the UV-filter and down-conversion luminescent material or simply using white LED lamps in laboratory studies; 2) strengthening the perovskite/ETL interface to resist the UV photocatalytic effect; 3) blocking the photocatalytic effect through inserting an interface with no photocatalytic activity; and 4) replacing the TiO$_2$ (SnO$_2$) by other ETLS with inferior or no photocatalytic activity.

#### 4.1. Using White LED lamps

Various reports have shown that the stability of these devices was assessed under different light sources. These include xenon arc,[46–47] metal halide,[48] sulfur plasma,[49] tungsten halogen, and combinations of LED lamps.[25,50,51] Among them, only xenon arc and metal halide emit a significant amount of UV radiation and their emission spectrum can be tuned to match the actual daylight spectral distribution. Based on our survey of the reported long-term stability profiles, most studies using TiO$_2$ or SnO$_2$ as ETLS used white LEDs to monitor device stability. It infers the importance of avoiding the photocatalytic activity of MO for stable operation of PSCs. The work by Burschka et al. was the first demonstration that MAPbI$_3$-sensitized TiO$_2$ solar cells are stable up to 500 h (20% decay in PCE) in argon atmosphere and under maximum power point (MPP) tracking, using a white LED with 100 mW cm$^{-2}$. Up to now, using a white LED to assess the photo-stability of PSCs is the means in the laboratory studies.

#### 4.2. Filtering UV Light

The commercial UV filter can effectively filter the UV light between 275 and 400 nm that cannot be absorbed by the Earth’s atmosphere. Using a UV filter has been a general and simple strategy that avoids inducing the photocatalytic activity of TiO$_2$ and SnO$_2$. To date, most PSCs can only work stably under illumination with UV filters. With the application of the UV filter, PSCs have achieved lifetimes of 10 000 h under simulated AM 1.5 G solar illumination at a stabilized temperature of 55 °C (Figure 4a), which is equivalent to the total irradiation of 10 years of outdoor use in most of Europe.[52]

Another approach to eliminate the UV light to the MO layer is directly coating a UV absorber layer on front of the transparent electrodes, such as ITO or fluorine-doped tin oxide (FTO). Ding and co-workers introduced an optimal UV absorber (2-(2H-benzotriazol-2-yl)-4,6-bis(1-methyl-1-phenylethyl)phenol, UV-234) on the front side of the FTO glass to filter the UV light.
between 300 and 400 nm (Figure 4b,c). The device with a UV absorber layer exhibited an enhanced photostability as there was no PbI$_2$ peak at 12.71°/C14 after the UV aging test for 12 h (Figure 4d). However, the device lost 2.2% PCE mainly because of a 2.7% decrease in $J_{sc}$ (21.43 vs. 20.85 mA cm$^{-2}$) without the contribution of UV light to efficiency. TiO$_2$ nanoparticles/graphene nanodot (TiO$_2$ NPs/GND) composites were used as a UV absorber layer placed in front of the PSC. As shown in Figure 4e, GNDs with low oxygen concentration have resulted in the narrowed bandgap of TiO$_2$ through carbon doping or the presence of additional energy states, which lead to the enhanced UV absorption (Figure 4f). As a result, the PSC with the TiO$_2$ NPs/GNDs showed only 15% decrease after 100 h of UV irradiation, whereas the PSCs with the TiO$_2$ absorber layer and without a UV absorber degraded 70% and 92%, respectively. The related stability tests are summarized in Table 1.

### 4.3. Inserting an Interfacial Modifier

The interfaces can block the photocatalytic activity of TiO$_2$ and SnO$_2$ to prevent the perovskite decomposition and device efficiency loss. In the following sections, we will summarize several

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**Table 1. Summarization of PSCs light stability test conditions without and with UV light absorber (UA).**

| UV absorber | Absorb [nm] | Device structure | Light-soaking conditions | Stability results [maintains PCE] | References |
|-------------|-------------|------------------|--------------------------|-----------------------------------|------------|
| UV-234      | 300-400     | UA/FTO/c-TiO$_2$/MAPbI$_3$/Spiro/Au | Unsealed, High-pressure mercury lamp, 4 mW cm$^{-2}$, ambient environment, 25 h | Without: 0% | [53] |
| TiO$_2$ NPs | <350        | UA/FTO/c-TiO$_2$/SnO$_2$/MAPbI$_3$/Spiro/Au | UV lamp, 365 nm, 100 h | Without: 8% | [54] |
| TiO$_2$ NPs/GNDs NPs | <350 | UA/FTO/c-TiO$_2$/SnO$_2$/MAPbI$_3$/Spiro/Au | UV lamp, 365 nm, 100 h | With: 85% | |
types of interfacial materials which were inserted between these ETLs and the perovskite absorber. The reported interfacial modification materials and the related light stability tests, discussed in this review, are summarized in Table 2.

### 4.3.1. Inserting an Inorganic Interface

**MO Interface Layer:** Various MO interface layers have been reported. In the early stage, TiO₂ combined with other MO (such as MgO, PbO, SrO, a-SnO₂, CaTiO₃, Sb₂S₃, CdS, ZnS, ZnSe, CsCl, CsBr, CsI, SnO₂, SnO₂/NH₄Cl, FASnCl₅, PCBB-2CN-2C8, PCBDAN, PCBM:Bphen, SM) have been studied as interfacial layers. These materials can improve the stability of PSCs by forming a protective layer that shields the perovskite from environmental degradation. Table 2 provides a summary of these materials and their performance in light stability tests.

### Table 2. Summarization of PSC light stability test conditions without (Control) and with an interfacial modifier (Materials).

| Category               | Materials | Device structure                      | Light-soaking conditions | Maintains initial PCE | References |
|------------------------|-----------|---------------------------------------|--------------------------|------------------------|------------|
| Inorganic metal oxides | MgO       | FTO/c-TiO₂/m-TiO₂/MgO/Perovskite/Spiro/Au | UV irradiation, 3000 mW cm⁻², 10 min | C: 36% M: 46.2% | [55]       |
|                        | PbO       | FTO/c-TiO₂/Perovskite/PCBM/Ag          | Ambient air, ≈42 °C, ≈40% RH, 364 mW cm⁻², 180 min | C: ≈0% M: 60% | [56]       |
|                        | SrO       | FTO/c-TiO₂/m-TiO₂/SrO/Perovskite/Spiro/Au | 365 nm UV light, inert gas, 100 h, 1 sun | C: 34.4% M: 60% | [57]       |
|                        | a-SnO₂    | FTO/c-TiO₂/a-SnO₂/Perovskite/Spiro/Au | UV lamp, 50 mW cm⁻², dry air box, 30 h | C: 72% M: 90% | [58]       |
|                        | a-SnO₂    | FTO/c-TiO₂/a-SnO₂/Perovskite/Spiro/Au | UV lamp, 40 mW cm⁻², room temperature, dry air box, 60 h | C: 82% M: 97% | [59]       |
|                        | CaTiO₃    | FTO/c-TiO₂/m-TiO₂/CaTiO₃ /FAPbI₃/(MAPbBr₃)₁ₓ/(FAPbI₃)₁−ₓ/Spriro/Ag | UV-LED (373 nm), 50 mW cm⁻², oxygen flow | C: / M: / | [60]       |
| Inorganic sulfide materials | Sb₂S₃  | FTO/TiO₂/Sb₂S₃/MAPbI₃/CuSCN/Au       | Unsealed, AM1.5 G, 100 mW cm⁻², air, 12 h | C: ≈0% M: 65% | [42]       |
|                        | CdS       | FTO/c-TiO₂/m-TiO₂/CdS/Perovskite/Spiro/Au | Full sunlight, 1 sun, 12 h | C: 42% M: 77% | [61]       |
|                        | ZnS       | FTO/ZnO/ZnS/CsFAMA/Spriro/Au          | Sealed (graphene), UV lamp (365 nm), 25 °C, ≈70% RH, 500 h | C: 0.07%, 150 h M: 87% | [62]       |
|                        | ZnSe      | FTO/TiO₂ or ZnSe/MAPbI₃/Spriro/Au      | 5 mW cm⁻², 500 h | C: ≈60% M: 90% | [63]       |
| Inorganic halide materials | CsCl     | FTO/TiO₂/CsCl/MAPbI₃₋ₓ/CIₓ/Spriro/Au | UV lamp (365 nm), 364 mW cm⁻², 41 °C, 30% RH, 200 min | C: ≈0 M: >70% | [43]       |
|                        | CsBr      | FTO/TiO₂/CsBr/MAPbI₃/Spriro/Au         | Unsealed, UV lamp (365 nm), 523 mW cm⁻², 41 °C, 30% RH, 20 min | C: ≈0% M: 70% | [64]       |
|                        | CsI       | FTO/c-TiO₂/SnO₂/FAPbI₃/Spriro/Au       | Unsealed, UV lamp (365 nm), 36.4 mW cm⁻², 500 h | C: 88% M: 38% | [65]       |
|                        | F-TiO₂    | ITO/F-TiO₂/Perovskite/Spriro/Au       | Sealed, high-voltage mercury lamp (365 nm cutoff filter), 500 W, 30 °C, 80% RH, 26 h | C: ≈0% (10 h) M: 68% | [66]       |
|                        | SnO₂/NH₄Cl| FTO/SnO₂/NH₄Cl/MAPbI₃/Spriro/Au        | UV (365 nm), 100 mW cm⁻², 500 h | C: <10%,100 h M: 82% | [67]       |
|                        | FASnCl₅   | FTO/SnO₂/FAPbI₃/Spriro/Au              | Unsealed, AM 1.5, 1 Sun, xenon lamp (without UV filter), 450 W, 100 mW cm⁻², N₂, 500 h | C: / M: 90% | [1]         |
| Organic materials      | PCBB-2CN-2C8 | ITO/TiO₂/PCBB-2CN-2C8/Perovskite/Spriro/Au | Unsealed, ambient, natural sunlight 6 h per day, 45%-50% RH, 500 h | C: 5.6%, 120 h M: 60% | [73]       |
|                        | PCBDAN    | FTO/c-TiO₂/PCBDAN/MAPbI₃/Spriro/Au     | Unsealed, AM 1.5 G, air conditions, 20 min | C: 50% M: 90% | [74]       |
|                        | PCBM:Bphen| ITO/SnO₂/PCBM:Bphen/Perovskite/Spriro/Au | Sealed, ambient atmosphere, UV lamp, 100 mW cm⁻², (280-385 nm, 50 mW cm⁻²), 1100 h | C: ≈0%, 120 h M: 95% | [75]       |
|                        | SM        | ITO/TiO₂/SM/Perovskite/Spriro/Au       | UV light, N₂, 25 °C, 500 h | C: ≈0% M: 90% | [76]       |
as MgO, PbO, SrO, and so on) has been used to improve the device stability under UV irradiation. For example, Wang and co-workers introduced MgO or PbO as a surface modification layer into PSCs to block the contact of perovskite/TiO₂ and protect the perovskite from UV photocatalytic corrosion. They demonstrated that PbO could serve as perovskite crystal seeds and induce a dense and robust perovskite film, which results in superior UV stability. After recording the UV stability of devices under 364 mW cm⁻² UV light, the PCE of PbO PSCs maintained 60% of initial value within 180 min, which was better than that of bare TiO₂ cells. The SrO interlayer was also used to passivate the degradation sites at the perovskite/m-TiO₂ interface, which is illustrated using spatially resolved µ-photoluminescence (PL) (Figure 5b). The SrO-incorporated film exhibited almost no change in the PL peak intensity and peak position, which was attributed to the passivated degradation site. These devices with and without the SrO coating maintained 60% and 35%, respectively, of their initial efficiencies after 100 h of UV exposure. Moreover, Tavakoli et al. believed that a thin amorphous layer of SnO₂ (a-SnO₂) could shield the UV-induced charge transfer passes at the interface and improve the stability of the device under UV light. Consequently, the double-layer structures of c-TiO₂/a-SnO₂ ETL and m-TiO₂/a-SnO₂ ETL have been introduced to modify the interface energetics, resulting in improved charge collection and decreased carrier recombination in PSCs. Among them, the UV stability of m-TiO₂/a-SnO₂-based perovskite device was improved drastically compared with pure TiO₂, whereas the PCE loss was only 3% after 60 h exposure to a UV lamp (Figure 5c). In addition, the inorganic perovskite also has been used to modify TiO₂. The in situ modification protocol was proposed to form a compact CaTiO₃ layer on TiO₂, which hinders the penetration of H₂O/O₂ in the film. The CaTiO₃ layer not only retards the recombination between electrons in TiO₂ and holes in the perovskite due to higher energy level of the CB bottom than TiO₂, but also retards the photocatalysis activity of TiO₂ with less “−O₂−” (Figure 5d). However, the high sintering temperature (450 °C) of CaTiO₃ and lower conductive property than TiO₂ may limit their application.

Sulfide Materials: Ito and co-workers first introduced a blocking layer of Sb₂S₃ between m-TiO₂ and CH₃NH₃PbI₃ to enhance the stability against light exposure. Under UV irradiation, the holes generated in the TiO₂ CB can extract electrons from an I⁻ anion in CH₃NH₃PbI₃, resulting in perovskite crystal decomposition. With the Sb₂S₃ layer, the charge extraction process can be prohibited, which makes CH₃NH₃⁺ fixed in the perovskite crystal and improves UV light stability but results in the enhancement of the charge recombination and a decreased Vₘₚ. The MAPbI₃ PSCs without Sb₂S₃ interlayer deteriorated to zero efficiency within 12 h, whereas those with Sb₂S₃ maintained 63% of initial efficiency (Figure 5e). Similarly, a uniform CdS shell was coated onto the surface of an m-TiO₂ layer. CdS could suppress the intrinsic trap sites of TiO₂ originating from the oxygen vacancies, which create some energy levels lower than the ordinary CB level of TiO₂ and lead to charge losses by recombination. As a result, the proposed TiO₂/Cds PSCs achieved improved light stability, maintaining 77% of the initial efficiency after 12 h of full-sunlight illumination, while only 42% was retained for the TiO₂ PSCs. In terms of Cd-containing compounds, Cd²⁺ cations and SO₄²⁻ anions have also been used to deposit a CdS layer on the TiO₂ surface by a chemical solution technique. As a result, the device with passivated TiO₂ showed 20% performance loss, while the pristine TiO₂ device showed 60% performance loss after 60 h of illumination.

Zheng and co-workers converted ZnO surface into ZnS at the ZnO/perovskite interface through sulfidation (Figure 5f). A strong coordination between S and Pb²⁺ creates a novel pathway for electron transport and reduces interfacial charge recombination. It slightly reduced the ETL transmission in the range of 310–380 nm (UV region), which benefited obtaining better photostability. ZnS-based PSCs displayed an outstanding improvement of UV stability by retaining 87% of its initial PCE over 500 h under UV irradiation, compared with ZnO-based PSCs of 0.07%. As one of the chalcogen compounds, ZnSe is a direct bandgap material of 2.8 eV, enabling broad absorbance in the UV region, which retards the UV degradation of perovskite materials without obviously decaying light harvesting in the rest of the solar spectrum (Figure 5g). The thin layer of ZnSe cooperated with TiO₂ can effectively reduce the interfacial charge recombination and promote carrier transfer because of the cascading CB level. Finally, the ZnSe-based device exhibited superior stability under UV exposure.

Table 2. Continued.

| Category | Materials | Device structure | Light-soaking conditions | Maintains initial PCE | References |
|----------|-----------|-----------------|--------------------------|-----------------------|------------|
| PEIE     | FTO/TiO₂/MA₀.₇₅FA₀.₂₅PbI₃/Spiro/Au | UV (254 nm), 50 mW cm⁻², RT, argon, 100 days | C: 90%, M: 75% | [44] |
| MDACL₂  | FTO/c-TiO₂/m-TiO₂/MDACL₂+(FAPbI₃)₀.₇₅(MAPbBr)_0.25/Spiro/Au | Unsealed, MPP, AM 1.5 G, 100 mW cm⁻², without UV cut off, ambient conditions, 600 h | C: 90% | [80] |
| S-AVAI  | FTO/c-TiO₂/m-TiO₂/ZrO₂/S-AVA/MA₁₋ₓPbI₃/Spiro/Au | MPP, 55 °C±5 °C, 1000 h | C: 20%, M: stable, 9000 h | [21] |
| UVP     | ITO/SnO₂/UVP + perovskite/Spiro/Au | UV (365 nm), 60 mW cm⁻², RT, ambient, 9 h | C: 74%, M: 91% | [82] |
| Sunscreen | ITO/SnO₂/Sunscreen + perovskite/Spiro/Au | UVb 285 nm, 1.35 mW cm⁻² | C: 20% | [83] |
photostability, which retained 90% of their initial efficiency after aging for 500 h.

**Halide Materials:** The halides are raw materials for preparing perovskite light absorption layers.[65] Researchers found that the halide could enhance the contact of perovskite with TiO₂ or SnO₂ and suppress the interfacial recombination. Wang and co-workers studied the impact of CsBr or CsCl interface modifier for c-TiO₂.[43,66] As for CsBr modification, after 95 min UV aging of 523 mW cm⁻², the normalized absorbance for the perovskite film on glass without TiO₂ or on c-TiO₂/CsBr substrate was at 0.99, while the absorbance of the perovskite film on c-TiO₂ fell sharply to 0.85 (Figure 6a). The better UV stability can be attributed to CsBr located at the interface covering UV-induced catalytic reaction activity sites of TiO₂. Recently, the CsI–SnO₂ complex was used as an ETL for the stable PSCs by Xu et al.[67] However, they emphasized that the incorporation of Cs⁺ into the perovskite at the bottom interface enhances the resistance against UV illumination. As shown in Figure 6b, the PbI₂ peaks (28.2°) of the pristine perovskite belong to UV-induced decomposition after 500 h of UV aging, while part of the perovskite film’s color changes from black to yellow. The UV aging test results are shown in Table 2.

Fluorine (F) has the highest electronegativity among all elements. It has been reported that the incorporation of F anion...
(F<sup>-</sup>) in the perovskite layer led to passivation of both anion and cation vacancies of perovskite and consequently improved PSCs’ device efficiency along with enhanced thermal and environmental stability. TiF<sub>4</sub> was doped into a TiCl<sub>4</sub> precursor solution by a one-step nonhydrolytic sol–gel method to obtain in situ low-temperature solution-processed TiO<sub>2</sub> nanocrystals. TiF<sub>4</sub> with stronger Ti—F ionic bonds is much more stable than TiCl<sub>4</sub> because of the much larger electronegativity of F than chlorine (Cl). The formation of Ti—F bonds brings increased electron mobility, decreased density of electronic trap states, and inhibits the photocatalytic activity of TiO<sub>2</sub> due to preferentially binding of F atom onto the (001) facet of anatase TiO<sub>2</sub>. As the photocatalytic activity of TiO<sub>2</sub> is sensitively dependent on the exposed crystal-line facet and surface fluorine termination, the F doping-induced exposure of (001) facet is expected to weaken the photocatalytic activity of TiO<sub>2</sub>. Finally, the 12% F–TiO<sub>2</sub> device retained 68% of the initial PCE after 26 h of continuous UV irradiation, whereas PCE of the control device degraded to nearly zero after only 10 h.

Hang et al. introduced a uniform NH<sub>4</sub>Cl film on SnO<sub>2</sub>. A chlorine-rich mixed-halide perovskite MAPb<sub>x</sub>Cl<sub>3</sub>–x interlayer (ClMPI) was formed through halide exchange between MAPb<sub>x</sub> and NH<sub>4</sub>Cl (Figure 6c). It was demonstrated that ClMPI possessed excellent tolerance to photocatalysis owing to the strong Pb—Cl bond. After exposing the PSCs to 365 nm UV light with a high power of 100 mW cm<sup>−2</sup>, the ClMPI PSCs could retain over 82% of the original value after 500 h, while the control device showed a constant drop and reduced to <10% of its original value within 100 h (Figure 6d). During their MPP test, the ClMPI-based device can maintain >80% after 500 h in a nitrogen glove box under continuous 1 sun illumination without any UV filter (Figure 6e), which was two orders of magnitude improvement compared with the control devices (only 4 h).

Very recently, Seok et al. introduced an FASnCl<sub>x</sub> interlayer between SnO<sub>2</sub> ETL and perovskite layer, through coupling Cl-bonded SnO<sub>2</sub> (Cl-bSO) with a Cl-containing perovskite precursor. This interlayer can enhance charge extraction and transport from the perovskite layer, and fewer interfacial defects, which lead to a record PCE of 25.8%. The efficiency of PSCs based on a planar TiO<sub>2</sub> ETL (Cl–TiO<sub>2</sub>) decreased substantially over time, even within an hour, in contrast to those based on Cl–bSO. The main reason is the different number of bound Cl<sup>-</sup> ions at the interface. The long-term operational stability of the unencapsulated device was tested under MPP tracking without a UV cutoff filter. As a result, the device maintained roughly 90% of its initial efficiency after 500 h. They emphasized that interfacial binding between the perovskite and electrode in the planar structure had substantial influence on the stability, rather than being a unique property of SnO<sub>2</sub>.

4.3.2. Inserting an Organic Interface

The fullerene and its derivatives have excellent semiconductor properties and they were widely used as interlayers between MO and the perovskite to cut off the photocatalytic degradation
without compromising efficiency.[69–72] Li et al. studied the passivation of the c-TiO2 surface by a triblock-functionalized fullerene derivative [(6,6)-phenyl-C61-butyric acid-dioctyl-3,3’-(5-hydroxy-1,3-phenylene)-bis(2-cyanoacrylate) ester, PCBB-2CN-2C8): fullerene C60 ensures high electron affinity for efficient electron transfer; electron-deficient cyanogroups are used to pacify the oxygen vacancy.[73] The unencapsulated cells retained more than 60% of their initial efficiency after 500 h of exposure under natural sunlight (6 h per day) at humidity of 45–50% (Figure 7a). The amine-based fullerene derivative of fullerene [6,6]-phenyl-C61-butyric acid 2-((2-(dimethylamino)ethyl)(methyl)-amino)-ethyl ester (PCBDAN) was introduced as an interfacial modifier between c-TiO2 and perovskite layers.[74]

The fullerene derivative modification can passivate or eliminate the trap states at the TiO2 surface and suppress the decomposition of the perovskite. Snaith et al. used C60 as the n-type charge collection layer and used 4-(1,3-dimethyl-2,3-dihydro-1H-benzimidazol-2-yl)-N,N-diphenylaniline (N-DPBI) as a dopant to improve the conductivity and air stability of C60.[75] Thus, such a strategy could reduce the UV-induced degradation of the solar cell and enhance device efficiency with improved long-term device stability under simulated full-spectrum sunlight.

Unfortunately, the introduction of the fullerene used as an interlayer to block the photocatalysis effect of SnO2 usually leads to rapid initial degradation, which is known as a “burn-in” effect. Hang et al. found that introducing a small organic molecule bathophenanthroline (Bphen) can largely stabilize PCBM through forming thermodynamically stable complexes under UV and natural light soaking.[76] For the light-soaking test, these various types of devices were measured at 60 °C for 1000 h of continuous MPP tracking without any UV filter (Figure 7b). After light soaking, the PCE of the PCBM-based device maintained stabilized efficiency of over 70% of its initial efficiency, and the PCBM: Bphen-based device retained over 92%, which was far beyond the SnO2 device (only remaining <30% within 100 h). As shown in Figure 7c, the PCBM:Bphen device retained over 95% of its initial efficiency after 1100 h of the UV preconditioning test, which was far beyond the SnO2-based device (nearly zero) and exceeded the PCBM-based device (maintaining 70% of its initial PCE).

One of the natural selecting sunscreens of plants-sinapoyl malate (SM) as an ester derivative of sinapic acid has been used to modify the interface of TiO2/perovskite (Figure 7d).[77] The SM molecules formed a protonated model to accomplish the binding of SM2−– TiO2 (TiO2-SM), exhibiting a broader absorption spectrum below 400 nm and lower transmission in the range of 300–390 nm (Figure 7e), which decreases the destruction by UV radiation for PSCs. As a result, the PSC device with TiO2 showed rapid decomposition with almost whole performance decay within 500 h under UV illumination. In comparison, as expected, the cells with SM treatment retained over 90% of its original efficiency after illumination. In addition, polyethylenimine ethoxylated (PEIE) was proposed to improve the UV stability by blocking the transformation of Ti3+–Vo states (as mentioned earlier).

Figure 7. a) The efficiency evolution of devices with and without PCBB-2CN-2C8. Reproduced with permission.[73] Copyright 2015, American Chemical Society. b) Light-soaking test of the SnO2, SnO2/PCBM, and SnO2/PCBM:Bphen devices and c) long-term 365 nm UV stability. Reproduced with permission.[76] Copyright 2021, John Wiley and Sons. d) Schematic illustration of SM assembled at the interface between TiO2 and perovskite and e) transmission spectra of TiO2 films modified by SM. Reproduced with permission.[77] Copyright 2018, John Wiley and Sons.
The optimized devices maintained $\approx 75\%$ of its initial PCE (20.51%) under UV irradiation at 72 days, whereas the normal devices failed completely.

4.3.3. Component Optimization of Perovskite

In case of perovskite degradation, it has been analyzed by considering the local electric field which is generally the practical working condition for solar cells and often causes ion migration as it can accelerate the reaction between oxygen and perovskite in light conditions.\(^{[78,79]}\) Seok et al. introduced methylenediammonium dichloride (MDACl\(_2\)) for stabilizing the a-FAPbI\(_3\) phase based on a typical m-TiO\(_2\) structure.\(^{[80]}\) The optimized device maintained $\approx 90\%$ of its initial efficiency ($>23.0\%$) of over 600 h of full-sunlight illumination without UV cutoff. They attributed the excellent photostability to the high concentration of Cl ions in the TiO\(_2\)/perovskite interface and the stable black phase of a-FAPbI\(_3\).

Han et al. used the bifunctional organic molecular (5-ammoniumvaleric acid, 5-AVA) to inhibit the MAI loss at grain boundaries, crystal reconstruction, and irreversible ionic migration of MAPbI\(_3\) under multiple actions of light, heat, and electrical bias.\(^{[21]}\) It was illustrated that the ammonium groups and carboxyl groups of 5-AVAI make the perovskite grains connect with each other or connect the MO (Figure 8a). The printable PSCs filled with (5-AVA)\(_3\)MA\(_{1-x}\)PbI\(_3\) showed a slower attenuation process under the UV preconditioning test (Figure 8b) and they kept their performance after 1000 h of continuous light soaking at MPP (Figure 8c). Notably, a printable mesoscopic PSC passed IEC61215:2016 qualification tests with more than 9000 h of operational tracking, which indicates that the homologous crosslinking reaction between two selected molecules is a useful and meaningful approach to improve the PSCs’ stability.

A “sunscreen” strategy using a tautomeric molecule is also proposed to regulate the defect passivation and enhance UV photostability. 2-Hydroxy-4-methoxybenzophenone, having the hydrogen on hydroxyl and the adjacent oxygen on carbonyl, can act as a sunscreen UV absorber. The molecule was demonstrated to form stable coordination and restrain UV degradation by tautomeric transition (Figure 8d), which induces high defect formation energy ($\approx 1.35$ eV).\(^{[81]}\) It was demonstrated that the carbonyl groups form an intermediate adduct with PbI\(_2\). The sunscreen-based PSC exhibited excellent UV stability at 285 and 365 nm (Table 2). As a widely used UV absorber in the industry, 2-(2-hydroxy-5-methylphenyl)benzotriazole (UVP) was also used as an additive to PbI\(_2\).\(^{[82]}\) The incorporated UVP molecule absorbs UV through the opening and closing of the chelating ring. The comparisons of stability are presented in Table 2.

![Figure 8](https://example.com/figure8.png)  
**Figure 8.** a) Schematics for structures of MAPbI\(_3\) and (5-AVA)\(_3\)MA\(_{1-x}\)PbI\(_3\) with the process of materials decomposition and ionic migration under multiple actions of light, heat, and electronic bias. b) UV preconditioning test (50 kWh m\(^{-2}\)) and c) MPP light-soaking test of MAPbI\(_3\) and (5-AVA)\(_3\)MA\(_{1-x}\)PbI\(_3\). Reproduced with permission.\(^{[21]}\) Copyright 2020, Elsevier. d) Schematic illustration of the sunscreen PSCs. Reproduced with permission.\(^{[81]}\) Copyright 2021, John Wiley and Sons.
4.4. Replacing TiO\textsubscript{2} with UV-Inactive Materials

4.4.1. UV-Inactive Inorganic ETLs

Replacing TiO\textsubscript{2} by other semiconductor materials with inferior or even no photocatalytic effect can effectively improve the photostability. Snaith and co-workers showed replacement of the mesoporous n-type TiO\textsubscript{2} by an insulating mesoporous Al\textsubscript{2}O\textsubscript{3} scaffold.\cite{41} The result showed that the stability of the mesoporous Al\textsubscript{2}O\textsubscript{3} device was much better than that of the TiO\textsubscript{2} device under UV light. The encapsulated Al\textsubscript{2}O\textsubscript{3}-based solar cells with epoxy resin and a glass coverslip in a nitrogen-filled glove box display stable photocurrents under continuous full-spectrum sunlight for a period of over 1000 h (Table 3). Then, they used Al-doped TiO\textsubscript{2} to reduce the nonstoichiometric oxygen-induced defects in TiO\textsubscript{2}.\cite{83} This type of Al(III) substitutional doping combined with oxygen vacancies does not introduce defect energy levels in the bandgap because of the stable threefold coordination of Al(III). The stability enhancement is attributed to the substitutional incorporation of Al in the anatase lattice.

| Classification                  | Materials\textsuperscript{a} | Device structure             | Light-soaking conditions                  | Maintains initial PCE | References |
|---------------------------------|-------------------------------|-------------------------------|------------------------------------------|------------------------|------------|
| UV-inactive inorganic materials | Al\textsubscript{2}O\textsubscript{3} | ITO/TiO\textsubscript{2}/MAPbI\textsubscript{3}, Cl\textsubscript{x}/Spiro/Au | Sealed, Xenon lamp, 76.5 mW cm\textsuperscript{-2}, N\textsubscript{2}, 40 °C, 1000 h | C: 15% 4 h M: stable | \cite{41} |
|                                 | α-Fe\textsubscript{2}O\textsubscript{3} | FTO/TiO\textsubscript{2}/MAPbI\textsubscript{3}/Spiro/Au | Unsealed, mercury lamp, 365 nm, 500 mW cm\textsuperscript{-2}, air, 1 h | C: 40% M: 85% | \cite{87} |
|                                 | Ni:α-Fe\textsubscript{2}O\textsubscript{3} | ITO/TiO\textsubscript{2}/MAPbI\textsubscript{3}/Spiro/Au | Mercury lamp, 220 min | C: 0% M: 60% | \cite{86} |
|                                 | α-Fe\textsubscript{2}O\textsubscript{3} (NSGQDs) | ITO/TiO\textsubscript{2}/MAPbI\textsubscript{3}/Spiro/Au | 500 mW cm\textsuperscript{-2}, 300 min | C: 0% M: 94% | \cite{88} |
|                                 | Nb\textsubscript{2}O\textsubscript{5} | FTO/TiO\textsubscript{2}/Perovskite/Spiro/Au | Sealed, 365 nm LED, 46 mW cm\textsuperscript{-2}, 10 h =40% RH | C: 40% M: 93% | \cite{87} |
|                                 | La:BaSnO\textsubscript{3} | FTO/TiO\textsubscript{2}/MAPbI\textsubscript{3}/Spiro/Au | Sealed, metal-halide lamp, AM 1.5 G (UV), air, 1000 h | C: 0% M: 93.3% | \cite{48} |
|                                 | ZnTiO\textsubscript{3} | ITO/TiO\textsubscript{2}/Perovskite/Spiro/Au | Unsealed, UV light (365 nm), 8 mW cm\textsuperscript{-2}, 100 h | C: =50% M: 90% | \cite{92} |
|                                 | 2D Ti\textsubscript{1-δ}O\textsubscript{2} | FTO/TiO\textsubscript{2}/MAPbI\textsubscript{3}/Spiro/Au | UV light, 5 h | C: 0% M: 68% | \cite{93} |
|                                 | 2D TiS | FTO/TiO\textsubscript{2}/MAPbI\textsubscript{3}/Spiro/Au | UV light, 10 h, 8 mW cm\textsuperscript{-2} | C: 56% M: 90% | \cite{94} |
| 1D TiO\textsubscript{2} nanocolumns | ITO/TiO\textsubscript{2}/Perovskite/Spiro/Au | Unsealed, UV light (365 nm), 3 mW cm\textsuperscript{-2}, argon, 95 h | C: 50.1% M: 92.3% | \cite{95} |
| UV-inactive organic materials   | Li-C\textsubscript{60} | FTO/TiO\textsubscript{2}/MAPbI\textsubscript{3}/Spiro/Au | Unsealed, 365 nm, 1 mW cm\textsuperscript{-2}, 50 °C, 45% RH, air, 300 min | C: 25% M: ~100% | \cite{123} |
|                                 | Co\textsubscript{90}/ultrathin-TiO\textsubscript{4} | ITO/TiO\textsubscript{2}/MAPbI\textsubscript{3}/Spiro/Au | UV 340 nm, 10 mW cm\textsuperscript{-2}, 30 °C, =45% RH, 312 h | C: 0% M: 83% | \cite{99} |
|                                 | C\textsubscript{60}/C\textsubscript{60}-nanoparticles | ITO/c-TiO\textsubscript{2}/m-TiO\textsubscript{2}/MAPbI\textsubscript{3}/Spiro/Au | Unsealed, 1 mW cm\textsuperscript{-2}, UV 365 nm, 25 °C, 40% RH, 1200 h | C: 0% M: 90% | \cite{96} |
|                                 | PCBM-GQDs | ITO/PCBM/MAPbI\textsubscript{3}/Spiro/Au | Unsealed, A.M 1.5 G, glove box, 300 h | PCBM: <50% PCBM: 80% | \cite{102} |
|                                 | PCBM:PCBDAN | ITO/TiO\textsubscript{2}/MAPbI\textsubscript{3}/Spiro/Au | Unsealed, 365 nm, N\textsubscript{2}, 190 mW cm\textsuperscript{-2}, 240 h | C: 30% M: 85% | \cite{97} |
|                                 | PCBM:C\textsubscript{60}/PFN | ITO/TiO\textsubscript{2}/MAPbI\textsubscript{3}/Spiro/Au | AM1.5 G, full spectrum, in a glove-box, 1200 h | C: 0% M: 63% | \cite{103} |
|                                 | PFN-2TNDI | ITO/TiO\textsubscript{2}/MAPbI\textsubscript{3}, Cl\textsubscript{x}/Spiro/Au | Sealed, 365 nm, argon glove-box, 3000 h | C: <10%, 300 h M: 75% | \cite{104} |
and holes, as well as low diffusion lengths of holes, which could be beneficial for superior UV stability. In comparison with the TiO2, α-Fe2O3 (≈2.3 eV) with a narrow bandgap causes parasitic light absorption in the visible light region below 600 nm.[85,86] The use of a compact α-Fe2O3-discrete α-Fe2O3 nanoisland structure builds some gaps, which ensure visible light transmittance utilized by the perovskite layer and enhanced UV light absorption.[87] Then, Ni-doped and N, S codoped graphene quantum dots (NSGQDs) were sequentially used for Fe2O3-based PSCs,[88] which improved the electron conductivity and tailored multiple interfaces, respectively, as well as UV light stability (Figure 9a).

Nb2O5 has high optical transparency, chemical stability, outstanding conductivity, as well as matched energy levels to perovskites, and it has been used in both dye-sensitized solar cells and PSCs by the sputtering technique.[89] Wang et al. reported a low-temperature solution route to prepare Nb2O5 nanoparticles and further utilized them as ETLs (Figure 9b).[90] The Nb2O5 nanoparticles show much better anti-UV ability due to better chemical stability, which suppressed the UV light-induced O2− (as mentioned earlier) and showed improved UV-stable perovskites. The normalized Jsc of unencapsulated PSCs was recorded upon UV exposure (Figure 9c). Devices based on Nb2O5 can retain 93% of their initial Jsc, whereas those devices based on TiO2 can only retain 40% of their initial Jsc. Finally, PSCs with improved UV stability were obtained by replacing TiO2 with Nb2O5 (Table 3).[90]

Some perovskite-structured semiconductors have been used as an UV-inert ETL, but the high crystallization temperature (>1000 °C) inhibits their application on glass substrates.

Figure 9. a) Normalized PCE decay of perovskite devices based on different ETLs as a function of UV irradiation time (500 mW cm−2). Reproduced with permission.[88] Copyright 2020, American Chemical Society. b) Degradation diagrams of Nb2O5- and TiO2-based PSCs upon UV exposure and c) normalized Jsc of Nb2O5 and TiO2-based PSCs. Reproduced with permission.[90] Copyright 2019, American Chemical Society. d) ZTO particle, e) the photocatalytic degradation of MB on different catalysts under full-spectral light, and f) photostability tests under UV illumination for PSCs based on ZTO and TiO2 ETLs. Reproduced with permission.[92] Copyright 2019, John Wiley and Sons. g) PSC structure containing 2D Ti1−xO2 as an ETL, and h) the effects of UV irradiation on carrier dynamics of c-TiO2 and 2D Ti1−xO2: amplitude (ΔArec) correlates with the number of carriers relaxed through recombination. Reproduced with permission.[122] Copyright 2019, American Chemical Society.
La-doped BaSnO₃ (LBSO) has high electrical mobility (320 cm² V⁻¹ s⁻¹) at room temperature as well as inferior UV photocatalytic ability because of its small dipole moment, ascribed to the cubic perovskite structure without octahedra tilting. Seok et al. first obtained a compact, crystalline LBSO thin film below at least 500 °C by a crystalline superoxide–molecular cluster colloid solution.[91] The monitored PCEs of the encapsulated devices were tested with a metal–halide lamp, including UV radiation. The TiO₂-based device completely degraded within 500 h, whereas the LBSO device maintained 93.3% of the initial PCE value after 1000 h (Table 3), which showed superior resistance against photodegradation.

ZnTiO₃ (ZTO) is a perovskite-structured semiconductor material with a wide bandgap (3.25 eV), excellent chemical stability, and poor photocatalysis. Wei et al. introduced ZTO as a UV-inert ETL to improve light stability (Figure 9d).[92] The photocatalytic activity of ZTO and TiO₂ was evaluated by the photocatalytic degradation of methylene blue (MB) aqueous solution under full-spectrum light irradiation in Figure 9e. MB drastically degraded by TiO₂ (70% loss after 20 min), while the ZTO sample has low photocatalytic activity on MB molecules (15% loss after 50 min). In contrast to the TiO₂-based device with fast degradation, the ZTO-based device maintained 90% of its initial value after 100 h. The PCE evolvement of the device under UV light (365 nm) is shown in Figure 9f, showing the UV-inert property of this interface.

Low-dimensional materials have been used as ETLs in PSCs owing to their superior mechanical and electrical properties. The novel 2D atomic sheets of the titania (Ti₁₋ₓO₂) layer (ASTL) were prepared by solution-processed atomic layer-by-layer deposition technique (Figure 9g).[93] As the 2D titania atomic sheets possessed the unique properties of high UV transparency and negligible oxygen vacancy, the device exhibited excellent UV stability as compared with that consisting of a conventional c-TiO₂ ETL. As shown in Figure 9h, upon UV light exposure, the recombination number (ΔArec) substantially increased by nearly 100% for the compact TiO₂ ETL, whereas it remained nearly constant in devices with the 2D Ti₁₋ₓO₂ ASTL. The major property that differentiates UV sensitivity indicated that less photogenerated electrons and holes recombined at the perovskite/Ti₁₋ₓO₂ ASTL interface. Similarly, the 2D TiS₁ layer also exhibits lower photocatalytic activity due to the higher UV transparency and less sulfur vacancies.[94] In addition, a series of 1D TiO₂ nanocolumn photonic structures has been used as ETLs and these vertically aligned nanocolumn arrays exhibit better optical absorption in the UV spectrum compared with c-TiO₂, in particular in the wavelength range of 300–370 nm.[95]

4.4.2. Organic Semiconductor Materials

Some nonmetallic oxides are potential replacements for MO as they achieve long-term light stability in both rigid and flexible PSCs. For example, the carbon-based material family, including fullerene (C₆₀) and their derivatives (PCBM), graphene, graphene QDs, etc.,[73,96,97] has inspired much research effort (Table 3).

Fullerenes and their derivatives are among the most widely used n-type materials in organic electronic devices as they have both a suitable energy-level alignment and superior electron mobility.[98] They can also reduce the trap density, passivate grain boundaries of perovskite films, as well as lead to higher UV light stability of PSCs in contrast to m-TiO₂. To realize high-efficiency and UV-stable C₆₀-based PSCs, the Li-TFSI-doped C₆₀ or C₆₀/ultrathin-TiO₂ (C₆₀/u-TiO₂) bilayer was sequentially designed as a compact ETL by Liu et al.[99] The modified C₆₀ maintained less interfacial charge accumulation and excellent charge extraction at the electrode interface and significantly enhanced UV stability, as illustrated by Mott–Schottky (MS) plots (Figure 10a–c). Before UV illumination, the different ETL-based devices had the same order of magnitude (10⁻⁶). After UV illumination, the slope of the C₆₀-based device (~8.24 × 10⁻¹¹) and TiO₂-based device (~3.28 × 10⁻¹⁰) changed to be lower than the C₆₀/u-TiO₂ device (~1.85 × 10⁻¹²). The higher slope of the C₆₀/u-TiO₂-based devices indicates less interfacial charge accumulation and excellent charge extraction upon UV irradiation. Finally, the C₆₀/u-TiO₂ bilayer, C₆₀-based, and TiO₂-based PSCs retained 83%, 61%, and 0% of their initial performance after 312 h of UV irradiation, respectively.

PCBM is one of the most usual types of organic ETLs, which is generally used to obtain hysteresis-free n–i–p PSCs.[100,101] A low doping ratio of graphene QDs (GQDs) has been used to increase the low conductivity of PCBM to 0.422 mS cm⁻¹ because of the long electron lifetime and ultrafast electron extraction. It was noted that GQDs could fill the electron traps that originated from the dimerization of PCBM upon light exposure, which minimizes the negative impact on PCBM dimerization.[102] As shown in Table 3, the device with PCBM:GQDs maintained >80% of its original value under continuous full-spectrum sunlight over 300 h, which is about 1.5 times than the control device. As for amine-based fullerene, PCBDA has also been investigated to modify PCBM by a simple self-organization method. After 240 h of UV light soaking (190 mW cm⁻²), the devices with PCBM:PCBDA ETls maintains 85% of its original efficiency, whereas the TiO₂-based device only maintained ≈30%.

Subsequently, a low-temperature (~100 °C) prepared ternary ETL: C₆₀ and self-organized PFN (poly [(9,9-bis(3'-N,N-dimethylamino)propyl)-2,7-fluorene]-alt-2,7-(9,9-dioctyfluorene)] to PCBM (PCBM:C₆₀/PFN) are shown in Figure 10d.[103] The C₆₀ additive is incorporated to effectively improve the conductivity of the ETL and the PFN is used to decrease the energy barrier at the ITO/ETL interface and improve the stability under full-sunlight illumination. Notably, the device based on PCBM:C₆₀/PFN in Figure 10e shows slower degradation than the TiO₂-based device during 1200 h of full-spectrum illumination. As one of the copolymer ETLs, the amino-functionalized copolymer semiconductor PFN-2TNDI has a conjugated backbone consisting of fluorine, naphthalene diimide, and thiophene spacers.[104] When recording the UV-light aging process (365 nm) in an inert-gas atmosphere, the PFN-2TNDI-modified devices showed a much slower decay than that based on bare TiO₂ upon 3000 h (Figure 10f).

4.5. Downshifting Materials

The downshifting (DS) materials can efficiently absorb the UV photons and re-emit visible light that can be harvested by the photoactive layer.[105–108] Theoretically, the DS materials can...
not only reduce the destructive effect of UV on PSCs but also improve the performance of the devices.\cite{106,107} The related parameters, discussed in this review, are summarized in Table 4. In 2016, the photopolymer V570-doped (fluorescent organic dye) fluoropolymeric layer has been coated on the front side of the PSCs.\cite{109} The DS coating converts the UV range into visible light, which increases the photocurrent by 6% and prevents UV light from interacting with the perovskite. During the device stability test, the all-front-coated cells devices kept in an Ar-filled dry glove box and irradiated 8 h per day with a UV optical fiber lost 2% of their initial PCE after 3 months; in comparison, the uncoated cells dropped nearly to zero. After that, developing such routes that effectively harvests the short-wavelength UV light and converts it into lower-energy photons of the absorption spectrum of the perovskite layer has been extensively studied.

Rare-Earth ions (such as Ce and Eu) have a charge transfer absorption band in the UV region, and their emission spectra are mainly located in the visible region.\cite{110-112} Thus, those are commonly used as the luminescence center to enhance PSC performance and stability.\cite{105} Rare lanthanide elements come into the view of DS materials as lanthanide complexes, which possess broadband absorption in the UV region and can effectively transfer the absorbed UV energy to lanthanide ions. One of the most efficient downconverting ions is europium (Eu\(^{3+}\)), as it has high-emission intensity.\cite{112} Ling et al. provided a modified sol–gel method to obtain downconverted TiO\(_2\):Eu\(^{3+}\) nanocrystal.\cite{113} In the mesoporous TiO\(_2\):Eu\(^{3+}\) structure, Eu\(^{3+}\) ion is the luminescence center and the UV light absorption of TiO\(_2\) nanocrystals can induce luminescence of Eu\(^{3+}\). The effective use of UV light showed an improvement of 29.2% from 12.22% to 15.79% in PCE. The same group also matched Eu\(^{3+}\) ion with a phenanthroline derivative ligand (4,7-diphenyl-1,10-phenanthroline).\cite{114} The formed Eu complex has been coated on the reverse of FTO (Figure 11a), displaying an enhancement of short-circuit current and PCE due to wide UV absorption (300–380 nm) and re-emitting in the visible range (Figure 11b). When exposed to UV light at 320 nm, the Eu complex layer emitted red light (inset of Figure 11b) and exhibited excellent downconversion fluorescence emission properties. Under the UV light-soaking test, Eu complexes acted as UV block layers and improved the maintained PCE from \(\approx 50\%\) to \(\approx 62\%\) after 10 h of UV illumination.

Similarly, Eu\(^{2+}\) has also been used to form a phosphor material and it can replace a fraction of Sr sites, forming SrAl\(_2\)O\(_4\):Eu\(^{2+}\), Dy\(^{3+}\) (SAED). Cong et al. used the pulsed laser deposition approach to build a mesoporous SAED scaffold layer between c-TiO\(_2\) and the perovskite layer, which avoids chemical ligands involved in nanomaterial synthesis.\cite{115} The calculated UV light harvesting of the SAED-based film increases by 82% compared with the bare film due to the transition from the 5d to 4f level of Eu\(^{2+}\),\cite{20} and it exhibits an emission in the green light region (Figure 11c). After UV irradiation, the devices with and without SAED maintained 92% and 40% of the initial PCE, respectively (Figure 11d). It demonstrates that SAED modification inhibited the light-induced deep trap states and the UV light-induced device degradation.

Some QDs have DS property with high PL quantum efficiencies (PLQE). CsPbCl\(_3\):Mn-based QDs were synthesized and applied onto the front side of the PSCs as the DS layer.\cite{116} The high
PLQE (60%) and large Stokes shift (>200 nm) of CsPbCl₃:Mn QDs can convert UV light into strong yellow emission (450–750 nm), as shown in Figure 11e. As a result, the CsPbCl₃:Mn-based devices showed increased $J_{sc}$ (3.77%) and the maintained PCE was also improved by 12% after soaking in UV irradiation for 100 h (Figure 11f). Furthermore, a thin layer of core–shell CdSe/CdS QDs (with 85% photoluminescence quantum yield) was placed on the back side of a device, which possessed a wide absorption region (300–500 nm) and could convert high-energy photons into low-energy photons (around 620 nm). Similarly, CdSe/ZnS QDs (PLQE of 85%) with green emission were proposed as ETLs for the first time. However, it needs a vacuum technique for perovskite film deposition to prevent the solvent to dissolve the underneath QD layer.

### 5. Conclusion and Perspective

Currently, all the state-of-the-art PSCs are generally based on the n–i–p conventional structure using TiO₂ or SnO₂ as ETL. One of the biggest challenges for these types of PSCs is that MO-based ETL causes photocatalytic activity under natural light and UV illumination. Although the phenomenon of photocatalysis-induced degradation is widely mentioned in numerous reports, only few studies have investigated the detailed degradation process and mechanism. Most results related to the degradation process and product were based on speculation rather than direct detection. More fundamental researches should be undertaken to deeply understand the origin of the photocatalytic degradation between the MO and perovskite, which can be a guide to develop a new strategy to solve this problem. We illuminate the main perspectives as follows. 1) Although the fundamental processes of TiO₂ and SnO₂ photocatalysis in liquid solution such as H₂O have been extensively studied, the photocatalysis process in the solid perovskite could be different. Therefore, more photochemical mechanisms and basic principles of photocatalysis based on the solid phase should be investigated, aiming to provide important information for restraining TiO₂ or SnO₂ photocatalysis under real PSC operation. 2) Only the separated electrons or holes in MO that migrate to the surface successfully have chances to drive the photocatalysis reactions. Therefore, it should be helpful to inhibit photocatalysis through accelerating the electron/hole recombination process in MO or reducing their diffusion to interface. 3) The influence of the actual operation environmental factors, including temperature, humidity, and electronic bias, on the photocatalysis process should be concerned and evaluated. These factors will largely affect the photocatalytic rate and thus PSCs stability. 4) Fundamentally, the stability of perovskite absorption layer under the photocatalysis of TiO₂ or SnO₂ is dependent on their component
and structure. Especially, uncovering the differences on the photocatalytic degradation among Cs, FA, and MA perovskites is significant to guide the design of perovskite compositions.

Photocatalytic degradation in MO-based cells could be simply inhibited by application of UV filters, but that would increase the additional cost of device production and seriously reduce the effective output by 10–20% due to the energy loss of the UV region when the device is in operation. It is known that solar cell efficiency is a key lever for PV cost reduction: a higher cell efficiency as high as 25%–30% can obviously reduce the cost performance of PSCs, which is generally regarded as a low-cost solar cell. Using inferior UV photocatalysis materials as HTLs can delay photocatalytic degradation; however, it is a still huge challenge to achieve efficiency as high as that of TiO2 or SnO2 PSCs. As for DS materials, light stability is still not fully understood or appreciated. It is difficult to compare the available results, mostly because of differences in the light source and measuring parameters. It is therefore challenging to reproduce and compare results and thereby develop a deep understanding of UV photocatalytic degradation mechanisms and the identification of various degradation factors.

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The authors declare no conflict of interest.

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