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Incorporation of Vanadium (V) Oxide in Hybrid Hole Transport Layer Enables Long-term Operational Stability of Perovskite Solar Cells

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ABSTRACT

Recent studies have shown that charge transport interlayers with low gas permeability can increase operational lifetime of perovskite solar cells serving as a barrier for migration of volatile decomposition products from the photoactive layer. Herein we present a hybrid hole-transport layer (HTL) comprised of p-type polytriarylamine (PTAA) polymer and vanadium (V) oxide (VO_x). Devices with PTAA/ VO_x top HTL reach up to 20% efficiency and demonstrate negligible degradation after 4500 h of light soaking, whereas reference cells using PTAA/ MoO_x as HTL lose $\sim 50\%$ of their initial efficiency under the same aging conditions. It was shown, that the main origin of the enhanced device stability lies in the higher tolerance of VO_x towards MAPbI_3 compared to the MoO_x interlayer, which tends to facilitate perovskite decomposition. Our results demonstrate that the application of PTAA/ VO_x hybrid HTL enables long-term operational stability of perovskite solar cells thus bringing them closer to commercial applications.

TOC GRAPHICS

Perovskite solar cells (PSCs) demonstrated rapid improvement in the light power conversion efficiency (PCE) since the first reported 3.8% in 2009¹ to the current record of 25.2%.² The technology owes this rapid progress to the simplicity of manufacturing of the absorber films using various processing techniques³, combined with the exceptional properties of the lead halide perovskite materials such as high absorbance, bandgap tunability, good charge transport properties and remarkable defect tolerance.⁴⁻⁶ Nevertheless, there are several obstacles to commercialization of PSCs⁷ with the insufficient operational stability being the most important among them.⁸

PSCs are comprised of $APbX_3$ absorber material with the perovskite crystal structure (where A is a univalent cation and X is halide anion) placed between charge transport interlayers that selectively extract and transport charges to the opposite electrodes. It is well documented now that lead halide perovskites incorporating organic cations can decompose with the formation of volatile byproducts under the action of stress factors such as elevated temperature, light, or electric bias.⁹ However, most of these decomposition reactions can be reversed if volatile components do not leave the active layer of the device, which can lead to at least partial restoration of the device efficiency in the dark e.g. during day/night cycling.¹⁰ Therefore, the most severe degradation pathways of PSCs can be suppressed if we block migration and loss of volatile aging products from the photoactive layer by using appropriate adjacent charge transport interlayers. In other words, charge transport interlayers have to function as encapsulation for perovskite absorber, so they are supposed to be composed of the materials with low gas-permeability. In case of conventional n-i-p PSCs architecture,¹¹ the hole-transport layer (HTL) deposited atop the perovskite absorber film plays the most crucial role. Metal oxides are known to have good barrier properties for volatile perovskite decomposition products. For example, using an ALD-grown SnO_2 electron-transport interlayer in combination with a 150 nm thick layer of ITO was reported to boost the stability of p-i-n devices at 85°C

for up to 1000 h.¹² Furthermore, the introduction of a bilayer composed of aluminum-doped zinc oxide (AZO) and SnO₂ layer under the metal electrode tends to preserve perovskite decomposition products in the structure leading to improved thermal and ambient stability.¹³ Using vanadium oxide as HTL component in n-i-p PSCs enabled decent efficiencies of up to 16.8% and provided reasonable device stability under ambient conditions and at elevated temperatures, while the operational stability of the devices under light exposure was not investigated.^{14–15}

Spectacular improvement in the operational stability of n-i-p PSCs was achieved by incorporation of just 15 nm of MoO_x oxide interlayer between organic HTL and the aluminum top electrode.¹⁶ In particular, non-encapsulated devices with MoO_x/Al electrode maintained 91% of the starting efficiency after 1000 h of continuous operation under 1 sun equivalent and using MPP tracking regime.¹⁷ However, such an impressive result was reached using low humidity (RH<20%) in combination with vigorous external device cooling to preserve the sample temperature at ~30°C. These results show that while using the MoO_x interlayer as HTL component greatly improves the operational stability of PSCs, the problem of heat sensitivity of this system still has to be addressed.

While this work was in preparation for publication, using VO_x as a more suitable replacement for MoO_x oxide interlayer in combination with a low molecular weight HTL material¹⁸ was reported at NanoGe conference.¹⁹ In particular, it was shown that MoO_x tends to delaminate and forms wrinkles at elevated temperature of 70°C, which was suggested to be the main reason for a drop in the current density of the degraded devices.

In this paper, we show that using MoO_x as HTL component is challenged by intrinsic properties of this oxide since it rapidly degrades lead halide perovskites at elevated temperatures on the contrary to vanadium pentoxide (VO_x), which was shown to be much less aggressive. The combination of VO_x with polytriarylamine (PTAA) enabled high efficiencies of n-i-p PSCs

approaching 20% and their much superior operational stability as compared to the reference cells comprising MoO_x/PTAA as HTL.

The concept pursued (Figure 1a) is based on the different nature of defects in organic and inorganic materials, therefore their combination is expected to have low gas permeability and good encapsulation properties, which are commonly exploited in designing plastic barrier foils. Both polymeric PTAA and inorganic VO_x films have relatively small roughness (Figure 1b–c), therefore, they can be combined to form the hybrid bilayer HTL. In addition, we expected that donor-acceptor interactions between the electron-deficient metal oxide and electron-rich amine centers in the polymer structure will enable excellent fusion between these two layers, while possible doping effects may also provide improved charge transport.

Figure 1. The concept of n-i-p PSCs with hybrid organic-inorganic HTL with low gas-permeability and excellent barrier properties with respect to the volatile perovskite decomposition products (a). Molecular structure of p-type transport polymer PTAA and topography of the spin-coated thin film of this material on glass (b). Linked pyramid-based structure and the topography of the evaporated 30 nm thick film of vanadium pentoxide on glass (c)

At the first stage of this work, the thickness of VO_x layer was optimized and it was shown that 30–45 nm deliver the best performance in n-i-p devices with the

ITO/SnO₂/PCBA/MAPbI₃/PTAA/VO_x/Ag configuration (Figure S1, Supporting information, SI). It should be emphasized that using single-layer HTLs based on either PTAA or VO_x leads to low device characteristics and poor reproducibility (Figure S2, SI). Therefore, combining inorganic and organic materials in one hybrid HTL is crucially important for reaching superior device performance.

Afterward, we explored the performance of PTAA/VO_x binary hybrid HTL in PSCs using a panel of different absorber and electron transport materials. The current-voltage (*J*-*V*) characteristics of devices with various configurations were obtained (Figure 2a–d, the configurations are shown in the insets). The current densities were confirmed with external quantum efficiency (EQE) spectra (Figure S3, SI), and the performance parameters reached for all studied configurations are summarized in Table 1.

Table 1. Characteristics of perovskite solar cells using VO_x as HTL component

Device configuration	V _{OC} , mV	J _{SC} , mA/cm ²	FF, %	PCE, %
ITO/SnO ₂ /PCBA ^(a) /CsFAPbI ₃ ^(b) /MAI ^(c) /PTAA/VO _x /Ag	average±standard deviation (top)			
	1021±47 (1044)	23.7±1.0 (24.6)	76±2 (78)	18.1±1.2 (20.1)
ITO/SnO ₂ /PCBA/MAPbI ₃ /PTA/PS ^(d) /VO _x /Ag	1029±12 (1032)	21.0±0.8 (22.1)	76±4 (80)	16.3±1.1 (18.3)
FTO/TiO ₂ /PCBM/CsFAPbI ₃ /PTA/VO _x /Ag	960±11 (974)	23.7±0.7 (24.0)	70±3 (76)	16.0±1.1 (17.7)
ITO/SnO ₂ /PCBA/CsFAPbI ₃ /PTAA/VO _x /Ag	994± (1009)	23.6± 1.8 (24.2)	58±6 (71)	13.1±2 (17.4)
ITO/ZnO/PCBA/CsFAPbI ₃ /MAI/PTA/VO _x /Ag	1022±9 (1027)	22.8±1.3 (23.0)	72±6 (75)	15.3±1.4 (17.7)
ITO/ZnO/PCBA/CsFAPbI ₃ /PTA/VO _x /Ag	1012±23 (1052)	22.0±2.4 (23.5)	53±7 (68)	10.4±2.0 (16.2)

a) PCBA –Phenyl C₆₁ butyric acid^{20, 21}, (Figure S4, SI); b) CsFAPbI₃ stands here and below for Cs_{0.12}FA_{0.88}PbI₃; c) MAI stand for CH₃NH₃I d) PS stands for polystyrene

Figure 2. Current-voltage characteristics of the devices comprising VO_x as a component of bilayer hybrid HTL

Devices comprising VO_x as an inorganic component of the hybrid bilayer HTL demonstrated good performances while using different perovskite formulations such as CsFAPbI_3 and MAPbI_3 , and various electron transport layer materials: ZnO , SnO_2 , TiO_2 combined with either PCBM or PCBA passivation coatings.²¹ It should be noted that PTAA was replaced in some cases by very similar PTA analog having fewer methyl groups (Figure S4, SI)²² and hence demonstrating improved charge transport characteristics. The best PCE was achieved for the device incorporating CsFAPbI_3 photoactive layer additionally covered with a thin layer of $\text{CH}_3\text{NH}_3\text{I}$ (MAI). According to the literature, such treatment leads to passivation of the defects at the grain boundaries of the perovskite material²³, which is also reflected in improved open-circuit voltage ($V_{\text{OC}} = 1035\text{--}1044$ mV, Figure 2d) compared to the cells with a similar configuration without MAI passivation ($V_{\text{OC}} = 990\text{--}1009$ mV, Figure 2b). Thus, the obtained results feature vanadium (V) oxide as highly promising and quite universal HTL material suitable for multiple types of PSCs.

At the next stage, we explored the impact of PTAA/VO_x hybrid HTL on the operational stability of n-i-p PSCs assembled using ZnO and CsFAPbI₃ as ETL and light absorber components, respectively (Figure 3a). While using Ag and Au top electrodes is preferable for achieving high power conversion efficiencies, it was shown that such electrodes might compromise device operational stability due to the tendency of these metals to diffuse and react with the lead halide perovskite.²⁴ Following previous reports, we used Al top electrodes, which slightly decreased the PSCs efficiency while contributing to their superior stability.^{16, 25} Thus, the best devices assembled in configuration ITO/ZnO/CsFAPbI₃/PTAA/VO_x/Al showed PCEs of 16.2 and 14.5% for reverse and forward scans, respectively (Figure 3b, Table 1).

The stability tests were performed using aging chamber integrated into the nitrogen-filled glovebox as described in detail previously (Figure 3a).^{9, 26} The samples were first exposed to the light of metal halide lamps (37 ± 3 mW/cm²) at the temperature of 45 ± 1 °C for 3200 h. Afterward, light soaking was continued for >1000 h using high-power LEDs as a light source (light flux 100 ± 3 mW/cm²) at the temperature of 50 ± 1 °C. No UV filters were used, while the devices were under open-circuit conditions throughout all aging experiment. The used aging conditions correspond to the recommended protocol ISOS-L-2I.²⁷ The evolution of the device efficiencies under illumination was collected (Figure 3c). The reference cells assembled using PTAA/MoO_x combination as HTL showed decent stability with ~24% drop in efficiency after 3200h under 30 mW/cm² and further ~25% decrease after 1300 h under 100 mW/cm². The observed accelerated aging at the second stage was due to higher light power and temperature, which is critical for PSCs assembled with MoO_x as it was mentioned above. The devices with PTAA/VO_x HTL have demonstrated spectacular stability: no efficiency loss within the first 3200 h of light soaking and relatively minor (~10%) decay after 1300 h at 100 mW/cm². Thus, the obtained results clearly indicate that VO_x enables much superior operational stability of PSCs as compared to MoO_x.

Figure 3. Stability of perovskite solar cells. Configuration of the devices and the experimental setup (a), the J - V characteristics of the best device (b), stability of perovskite solar cells with hybrid HTLs under illumination (c)

Improvement in operational stability of PSCs achieved by replacing MoO_x with VO_x might be attributed either to different phase behavior of their films as proposed recently¹⁹ or to the principally different chemical activity of these oxides towards the lead halide perovskites. In particular, previous studies suggested that MoO_x can facilitate MAPbI₃ decomposition and might be also aggressive to other complex lead halides.²⁸

Figure 4. Evolution of the absorption spectra of the glass/metal oxide/MAPbI₃ (a-b) and glass/metal oxide/PTAA/MAPbI₃ (c-d) samples at 75–80°C within 18 h in dark. Insets show photographs of MoO_x/MAPbI₃ (a) and VO_x/MAPbI₃ (b) films after 18 h of annealing.

To verify this hypothesis, we first investigated the behavior of glass/VO_x/MAPbI₃ and glass/MoO_x/MAPbI₃ stacks under thermal annealing at 75–80°C in dark. The rapid evolution of the absorption spectra of the glass/MoO_x/MAPbI₃ samples within 18 h and spectacular change of their color from dark brown to yellowish were observed (Figure 4a), thus evidencing poor thermal stability of this system. It is worthy to mention that the reference glass/MAPbI₃ samples showed no detectable aging under the same conditions, which proves that degradation of the glass/MoO_x/MAPbI₃ stacks is entirely due to the presence of MoO_x. On the contrary, glass/VO_x/MAPbI₃ samples were much more stable under the same conditions since no significant changes were observed in their optical spectra and visual appearance (Figure 4b).

Incorporation of thin (~20 nm) organic PTAA layer between MoO_x and MAPbI₃ slowed down the rate of the perovskite decomposition but failed to prevent it completely (Figure 4c). Finally, the glass/VO_x/PTAA/MAPbI₃ stacks showed no signs of degradation (Figure 4d), which explains why the PSCs using PTAA/VO_x material combination as HTL revealed superior operational stability. These results demonstrate that VO_x has good compatibility with perovskite absorbers on the contrary to MoO_x, which is quite aggressive and facilitates decomposition of lead halides most likely *via* redox pathway, due to a strong oxidizing nature of MoO_x reagent implicating its possible reaction with I⁻.

To summarize, in this work we introduced vanadium (V) oxide as a highly promising inorganic component of hybrid organic semiconductor/metal oxide HTLs delivering high efficiencies of up to 20% in n-i-p perovskite solar cells using various combinations of ETL and absorber materials. Most importantly, incorporation of VO_x as HTL component enables impressive operational stability of perovskite solar cells over few thousands of hours under continuous illumination. We also showed that faster degradation of the reference cells using MoO_x interlayer is associated with the aggressive chemistry occurring between this oxide and complex lead halides at elevated temperatures. On the contrary, VO_x was shown to be much more chemically inert with respect to the oxidation of the absorber material, which accounts for the observed largely increased lifetime of PSCs assembled using this oxide material. Finally, we strongly believe that the application of hybrid HTLs utilizing vanadium (V) oxide as an inorganic component (e.g. explored PTA(A)/VO_x systems) represents an important step towards increasing operational lifetime of perovskite photovoltaics which is essential for practical use of this technology.

ASSOCIATED CONTENT

Supporting Information Available: experimental procedures and figures S1–S4 with additional *J*-*V* characteristics and EQE spectra.

AUTHOR INFORMATION

The authors declare no competing financial interests.

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