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Interface passivation for perovskite solar cell: A good or bad strategy?

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The solution fabrication process has made perovskite solar cells attractive, but it generally causes abundant defects on the surface and grain boundaries of the perovskite layer. Surface passivation is the usual method to solve the problem, but it usually creates a negative work function, resulting in the potential well and charge accumulation. In a recent issue of *Nature*, Yang et al. developed a new surface passivation strategy to endow the counter-anion with the electron-withdrawing ability, resulting in champion power conversion efficiency and enhanced stability due to the suppressed ion migration.

Organic-inorganic perovskites have recently been regarded as promising photovoltaic materials due to their excellent photoelectric properties and low-temperature fabricability.[1–3] The power conversion efficiency (PCE) for perovskite solar cells (PSCs) has already achieved 25.7%, which is comparable to that of silicon solar cells.[4] However, defects can be readily generated within the grains, at the grain boundaries (GBs), and on the surface of the film due to their low formation energy, resulting in degradation in performance and stability, which has greatly slowed their commercialization.[5] Surface passivation with alkylammonium halogen, Lewis acid and base, etc. has been widely utilized to solve these problems.[2,6–8]

Recently, Yang and co-workers investigated the surface energetics of perovskite films.[9] The results show that the iodide-based ammonium surface treatments generally result in a negative work function change (ΔW) because of the electron-enriched surface. The electron-withdrawing anions such as bromide [Br]⁻, tetrafluoroborate [BF$_4$]⁻, trifluoroacetate [TFA]⁻, and tosylate [TsO]⁻ were employed to substitute the iodide [I]⁻, but only [TsO]⁻ with the strongest electron-withdrawing ability neutralized the negative ΔW. The Kelvin probe force microscopy (KPFM) measurements under illumination and open-circuit condition reveal that compared to the octylammonium iodide (OAI)-treated device (i.e., indium-doped tin oxide [ITO]/SnO$_2$/perovskite/Spiro-MeOTAD/Au), the octylammonium tosylate (OATsO)-treated device shows a negligible electron accumulation at the perovskite/Spiro-MeOTAD interface, which could

avoid the potential well and charge accumulation (Figure 1A). Interestingly, in another study, the photoluminescence (PL) spectra show that although the surface passivation could effectively suppress the charge-trapping defect states,[10] charge transport at the perovskite/Spiro-MeOTAD interface was also hindered in all surface-treated film with the similar trend of the ΔW. Compared with the reference/Spiro-MeOTAD films, the average carrier lifetime and steady-state PL intensity of the OAI-treated films largely increased. In contrast, the OATsO treatment simultaneously suppressed trap states and barely hindered the charge extraction (Figure 1B). Thus, the authors postulated that the charge obstruction and accumulation is not related to the surface 2D phase, since the insulating large organic cation (OA⁺) is kept unchanged. As a result, the power conversion efficiencies (PCEs) of the surface-treated devices show an order of OATsO-treated > OABF$_4$-treated > OAI-treated devices, mainly due to an increasing fill factor, and the best OATsO-treated device reached a PCE of 24.41%.
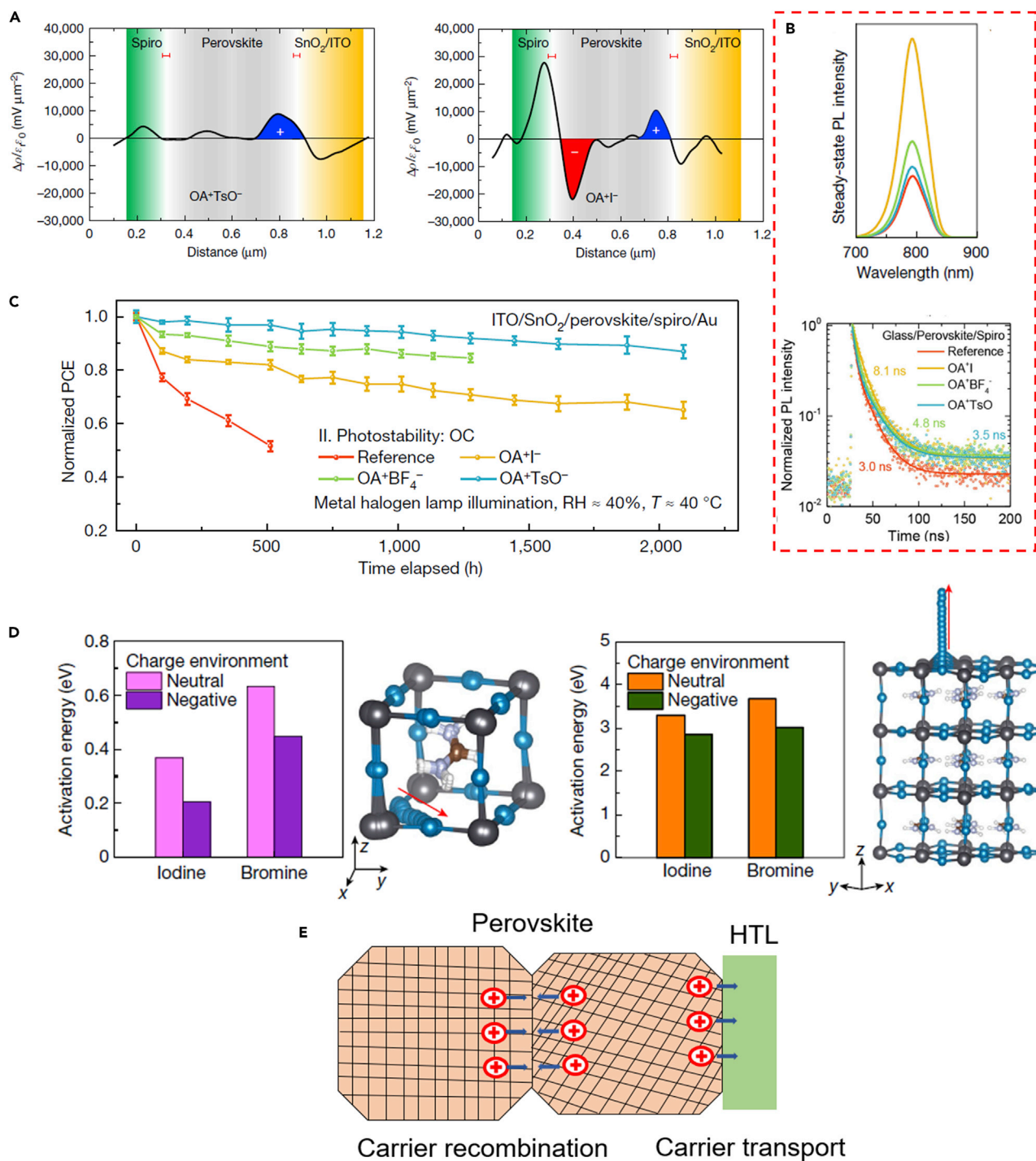
Figure 1. The performance and corresponding mechanism of PSCs with different passivation materials
(A) OATsO-treated and OAI-treated device cross-sections with KPFM.
(B) Steady-state and time-resolved PL spectra of the glass/perovskite/Spiro-MeOTAD films.
(C) Photostability of encapsulated devices aged under continuous illumination and open-circuit condition.
(D) Intra-lattice and extra-lattice migrations of halogen calculated using first-principles simulations.
(E) The carrier behavior of perovskite with passivation ($\Delta W > 0$). HTL: hole transport layer.
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Furthermore, the encapsulated devices with $CH(NH_2)_2PbI_3$ ($FAPbI_3$) as the light absorber were fabricated and aged in ambient atmosphere at -40°C (Figure 1C). The results reveal that the degradation trend for all devices is in line with ΔW change. After 2,092 h, the OATsO- and OAI-treated devices retained 87.0% and 65.1%, respectively, of their initial PCE on average. Thus, the authors assumed that the potential well and charge accumulation caused by the ΔW may have accelerated ion migration resulting in the poor stability. Scanning transmission electron microscopy was employed to investigate the hypothesis. Compared with the OATsO-treated devices, the OAI-treated devices manifest a rougher morphology at the perovskite/Spiro-MeOTAD interface and massive accumulations of both bromine and iodine at the electrode. Meanwhile, the first principles were utilized to explore mechanistic origins of ΔW and simulate the ion migration pathways. Ligand-induced ΔW originates from the ligand intrinsic dipole moment and a charge density displacement by ligand-surface interactions and bond formation. For intra-lattice and extra-lattice migration, the energy barriers for both iodine and bromine decreased substantially in the negatively charged environment (Figure 1D). Tying together all the results, the authors proposed that the potential well and charge accumulation created by a negative ΔW decreased the stability of device by accelerating halide migration.

In summary, this work systematically studied the effects of the interface energetics with passivation on the performance of the PSC devices. The traditional iodide-based ammonium as surface treatment material could introduce a negative ΔW on the perovskite surface, which would lead to charge accumulation at the interface and reduce the activation energy of halide ion migration in perovskite, thus limiting device stability. The counterions, such as TsO^-, could neutralize the negative ΔW, suppressing charge accumulation and ion migration. The work proposes design principles for the ideal perovskite/carrier transport material interface and opens a new route toward addressing the main obstacle to the practical application of perovskite devices.

However, there are still numerous defects on GBs of perovskite. The materials developed in the above work cannot be used to passivate the defects on GBs because it will cause severe carrier recombination by suppressing carrier transport among the grains (Figure 1E). The energy level inside the grains and on GBs of the light absorber should be consistent. Thus, passivation materials with the ΔW value = 0 should be employed to passivate the defects on GBs. The preparation of single-crystal perovskites is also a promising method to eliminate the GBs and avoid carrier recombination inside the light absorbers. We believe these strategies will further elevate the performance and facilitate the commercialization of PSCs.

ACKNOWLEDGMENTS

DECLARATION OF INTERESTS

The authors declare no competing interests.

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