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PERSPECTIVE

Designing Effective Hole Transport Layers in Tin Perovskite Solar Cells

Donghoon Song, Shripathi Ramakrishnan, Yuanze Xu, and Qiuming Yu*

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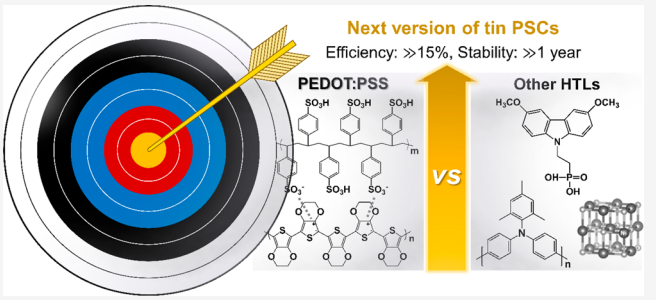
ABSTRACT: Beyond collecting hole charge carriers, hole transport layers (HTLs) in perovskite solar cells (PSCs) can play a significant role in determining the perovskite's quality and stability. While diverse prospective HTL materials are explored for high-performance lead-based PSCs, tin-based PSCs predominantly rely on poly(3,4-ethylenedioxythiophene) polystyrenesulfonate (PEDOT:PSS) to achieve power conversion efficiency near 15% and around 1 year of N_2 shelf-storage stability. While tin perovskites exhibit distinct characteristics in terms of crystal defect species, interfacial properties, crystallization mechanisms, and shallow energy levels, device architectures and HTL materials are usually adopted from lead PSCs without tailoring them for tin PSCs. In this regard, the effective design of HTLs in tin PSCs remains not well-explored. In this Perspective, we propose a comprehensive set of effective HTL design factors with a dedicated focus on tin PSCs, aiming at upgrading PEDOT:PSS and modifying other prospective HTLs to ultimately break the current performance limit to be competitive with or beyond lead PSCs.



Since their initial report in 2009, lead perovskite solar cells (PSCs) have undergone an unprecedented efficiency surge from 3.8% to >26%, marking a remarkable advancement in the history of photovoltaics. Since PSCs are now competitive in efficiency with commercialized crystalline silicon (c-Si) photovoltaics, researchers strive to realize their upscaling and sustainability for real-world applications. Representative efforts include replacing the environmentally hazardous lead with the eco-friendly element of tin in perovskites,[1] enhancing device stability for real-world operations,[2] developing materials and processes that are amenable to large-scale production,[3] and achieving efficiency breakthrough via tandem applications like c-Si/PSC systems.[4] Central to all of these efforts is the strategic design of effective hole transport layers (HTLs). Well-designed HTLs ensure prolonged and efficient hole collection without degradation, contribute to the high-quality perovskites, and are upscalable for commercialization. However, the design space for effective HTLs in tin PSCs is exceptionally narrow. While the overall research landscape of HTLs has been already dealt with in other review and perspective articles to enable the maturation of lead PSCs and the recent progress of tin–lead PSCs,[3−6] we herein aim to pinpoint essential factors and principal considerations and then propose our perspectives toward effectively designing HTLs for tin PSCs.

HTL RESEARCH LANDSCAPE IN LEAD AND TIN–LEAD PSCs

HTLs are an essential component in both n-i-p and p-i-n PSCs. Their excellent energy level alignment with perovskites is globally desirable for effective hole collections. Numerous HTLs are well-suited in energy levels to perovskites.[2−6] According to their chemical structure and composition, HTLs can be categorized into organic (small molecular, self-assembled monolayer (SAM), and polymeric) and inorganic materials. The highest occupied molecular orbital (HOMO) or valence band maximum (VBM) energy levels of representative HTLs that yield high-performance lead PSCs and the VBM energy levels of representative lead, tin–lead, and tin perovskites are presented in Figure 1.

High-performance lead PSCs with power conversion efficiency (PCE) > ∼25% have been achieved by using HTLs of small organic molecules such as 2,2′,7,7′-tetrakis-[*N*,*N*-di(4-methoxyphenyl)amino]-9,9′-spirobifluorene (Spiro-OMeTAD)[7] in an n-i-p architecture and by using other HTLs

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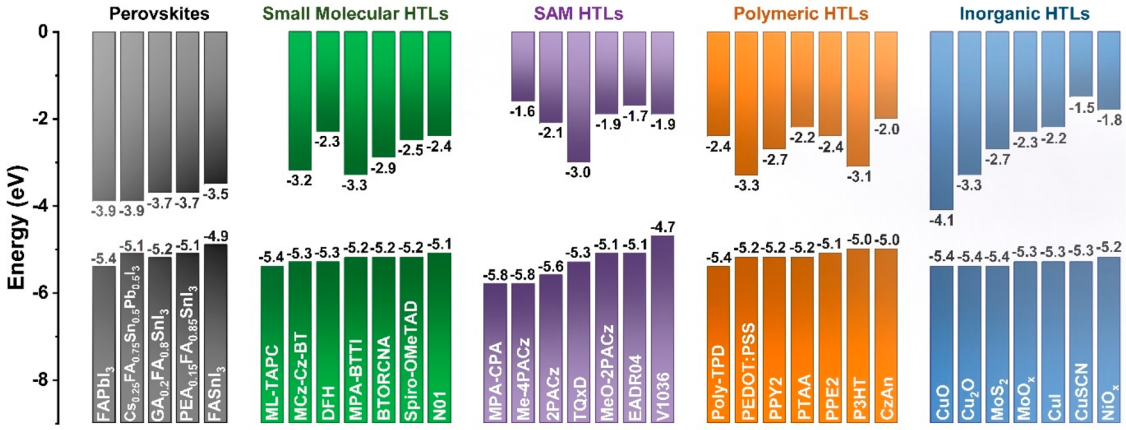

Figure 1. Energy level diagrams of 3D or quasi-3D and iodide-based perovskites and organic (small molecular, SAM, and polymeric) and inorganic HTLs. Bandgaps can serve as a guide to transparency, but additional factors such as refractive indexes, gap states, film structures, and so forth are influential. The energy level of the lowest unoccupied molecular orbital is unknown for ML-TAPC and MPA-CPA. The source of reference can be found in the Supporting Information.

of polymers such as poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine (PTAA)[8] and SAMs such as [2-(9H-carbazol-9-yl)ethyl]phosphonic acid (2PACz)[9] and [2-(3,6-dimethoxy-9H-carbazol-9-yl)ethyl]phosphonic acid (MeO-2PACz)[10] in a p-i-n architecture. Remarkably, they passed harsh condition tests needed for real-world operations. In specific, with PTAA and 2PACz HTLs, the lead PSCs successfully passed damp-heat testing for 1000 h at 85 °C and 85% relative humidity (RH).[8,9] They also endured repeated temperature cycling between −60 and 80 °C for 3000 h, with a MeO-2PACz HTL.[10] Many other organic HTLs such as small molecules (e.g., containing diphenylamine and triphenylamine moieties)[5] and conducting polymers (e.g., poly(3,4-ethylenedioxythiophene) polystyrenesulfonate (PEDOT:PSS) and poly(*N*,*N*′-bis(4-butylphenyl)-*N*,*N*′-bis(phenyl)benzidine),[5] and inorganic HTLs (e.g., nickel oxide (NiO_x) and copper thiocyanate (CuSCN))[6] have also been explored in lead PSCs to reach PCE > ∼20%. Especially, NiO_x delivered decent stability results under several real-world stressors including damp-heat testing, temperature cycling, and elevated illumination and temperature.[11,12] On the whole, a variety of HTL materials have been explored and proven to efficiently perform for lead PSCs.

Meanwhile, tin−lead PSCs attain low bandgaps (close to 1.2 eV), due to the band bowing phenomenon, for light harvesting in a wide spectrum in single junction devices and narrow bandgap sub-cells in tandems (e.g., PSC/PSC). Tin−lead PSCs have achieved better progresses than tin PSCs according to recent reports on high PCE (>20%) with diverse HTL materials including PEDOT:PSS,[13] NiO_x,[14] 2PACz,[15] and poly[(phenyl)imino[9-(2-ethylhexyl)carbazole]-2,7-diyl].[16] Moreover their shelf-storage for >1000 h is usually ensured,[13−16] although their operational stability particularly under real-world conditions has yet to be guaranteed and PCE should be further advanced in the future.

HTL RESEARCH LANDSCAPE IN TIN PSCs

In stark contrast, tin PSCs face significant limitations in the choice of HTLs. This is evident from the analysis of publications before and after the year 2020, depicted in Figure 2a. Four HTLs have been the focus in tin PSCs. Spiro-OMeTAD and PTAA are mostly used in n-i-p devices, while PEDOT:PSS and NiO_x are commonly utilized in p-i-n devices. Before 2020, PEDOT:PSS, Spiro-OMeTAD, and PTAA have been intensively explored. Increasing efforts have been devoted to modifying and optimizing PEDOT:PSS and NiO_x HTLs since 2020. Even though SAMs and other HTLs are emerging, PEDOT:PSS continues to be the dominate HTL in tin PSCs research, with approximately 70% of the total publications. Tin PSCs with the record efficiency and long shelf-storage stability typically contain PEDOT:PSS HTLs (Figure 2b,c).[17,18] Except for a few examples, even though other HTLs are endowed with lower PCE and stability (see Figure 2b,c and Summary of Energy Level and Device Performance.xlsx in the Supporting Information), they offer excellent HTL properties. For example, MeO-2PACz and PTAA render lower parasitic light absorption and hole transport losses and less hydrophilicity than PEDOT:PSS. As shown in Figure 2c, most of the stability tests are performed under stress-free conditions, like the N_2 shelf-storage. Current tin PSCs are facing a great challenge to pass harsh condition tests for real-world operations such as damp-heat testing and constant light illumination at high temperatures (>∼60 °C). Unlike lead perovskites, tin perovskites are subjected to rapid crystallization and easy oxidation from Sn(II) to Sn(IV), resulting in uncontrollable polycrystalline grain size and orientation as well as a large number of trap states, which are detrimental to device performance and stability. Therefore, designing effective HTLs for tin PSCs goes beyond the primary consideration of energy level alignment. The factors can be related to device architectures, interfacial properties, and/or perovskite crystallization, which we discuss in the following sections.

Even though self-assembled monolayers and other hole transport layers (HTLs) are emerging, PEDOT:PSS continues to be the dominate HTL in tin perovskite solar cells research, with approximately 70% of the total publications.

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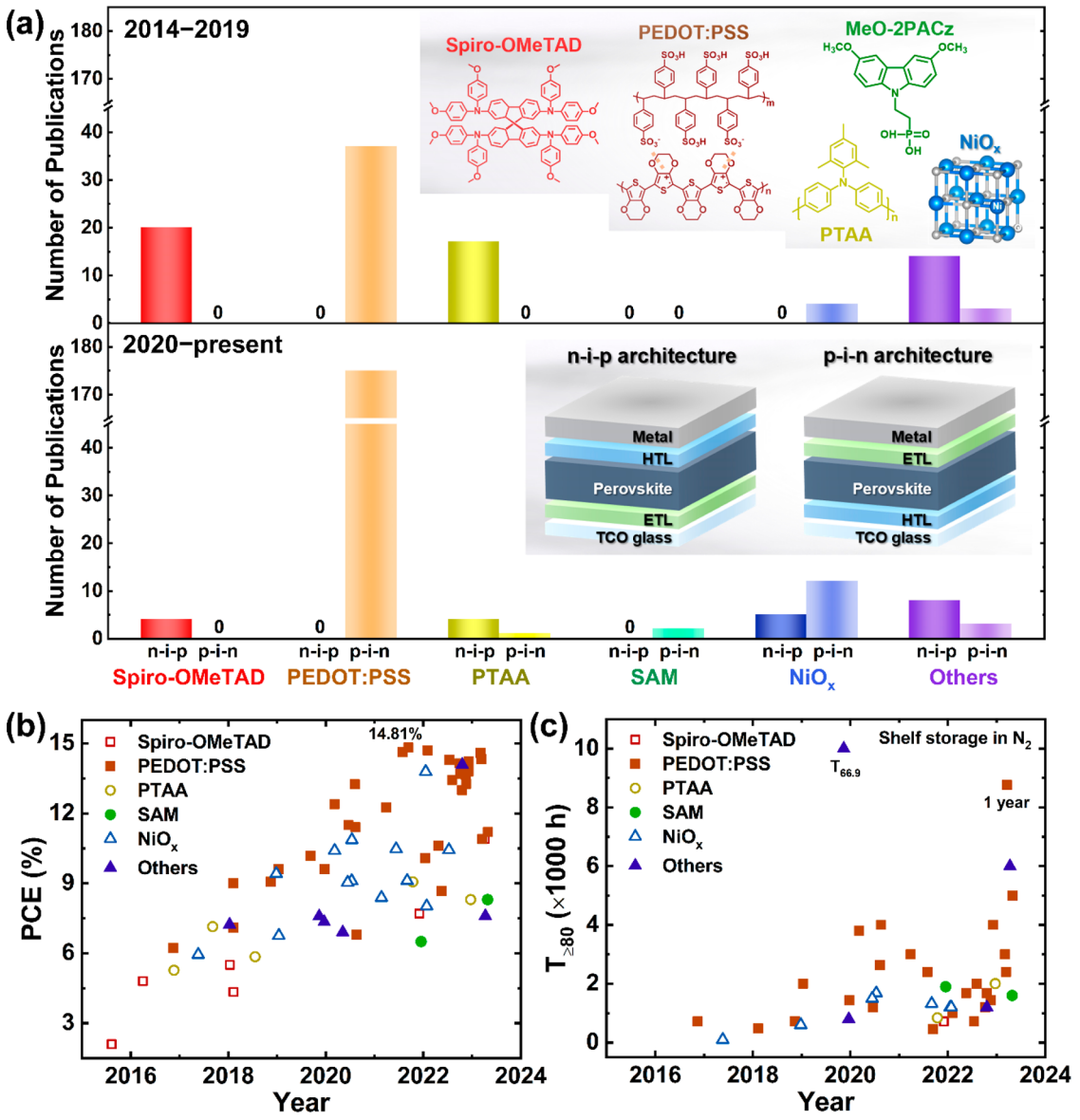

Figure 2. (a) The number of publications of different HTLs used in n-i-p and p-i-n tin PSCs during two consecutive time periods of 2014–2019 and 2020–present by 05/12/2023. Insets in the top and bottom panels are the chemical structures of representative HTLs and the n-i-p and p-i-n device structures, respectively. (b) PCE and (c) stability of tin PSCs with different HTLs versus publication year. Devices with 3D FA-based tin perovskites or analogs are chosen. For tin PSCs with PEDOT:PSS the representative high-performance devices in each year are selected. The PCE was evaluated under standard 1 sun illumination (AM 1.5G, 100 mW cm^{-2}). Some HTLs do not have stability data. $T_{\geq 80}$ stands for the time for ≥80% retention of the initial performance.

GENERAL HTL DESIGN FACTORS FOR PSCs

While HTLs are adjacent to the layers of tin perovskites either beneath or atop in the p-i-n or n-i-p architecture, respectively (Figure 2a), four general HTL design factors for PSCs are depicted in Figure 3a: 1) hole collection, 2) light absorption, 3) stability, and 4) processability. Three critical processes determine hole collection efficiency: hole transfer from the VBM of perovskite to the HOMO or VBM of the HTL, hole transport through the HTL, and hole recombination at the HTL/perovskite interface. To facilitate the transport, hole mobility $\mu_h > 10^{-5}$ cm^2 V^{-1} s^{-1} is a target.[5] Fast hole transfer (<∼1 ns) and slow recombination (≫1 ns) are highly desirable. Both can be affected by a hole charge carrier lifetime, energy level alignment, and interface defects.[19] Nonradiative recombination via deep traps must be avoided.[19] Appropriate energy offsets could suppress a thermionic loss for open-circuit voltage (V_{OC}). As the VBM of perovskite is shallower than the HOMO or VBM of a HTL, fill factor (FF) could be predominantly deteriorated.[20] Light absorption and reflection of HTLs should be regulated in order to maximize light harvesting of perovskite in a wide spectral window of ∼300–1000 nm. Besides low absorptivity $\alpha < 10^4$ cm^{-1}, morphology and thickness of HTLs are the factors to consider. Thinner HTLs (thickness ≈ 5–50 nm) are typically used in p-i-n devices while relatively thicker HTLs (thickness > ∼100 nm) are used in n-i-p devices. Close refractive indices between HTL and perovskite are preferred in p-i-n devices otherwise light reflection losses can be facilitated according to the Fresnel equation.[21] To deliver long-term operational stability, it is imperative that HTLs have high resistance and resilience to real-world stressors, including heat, light, and humidity, and

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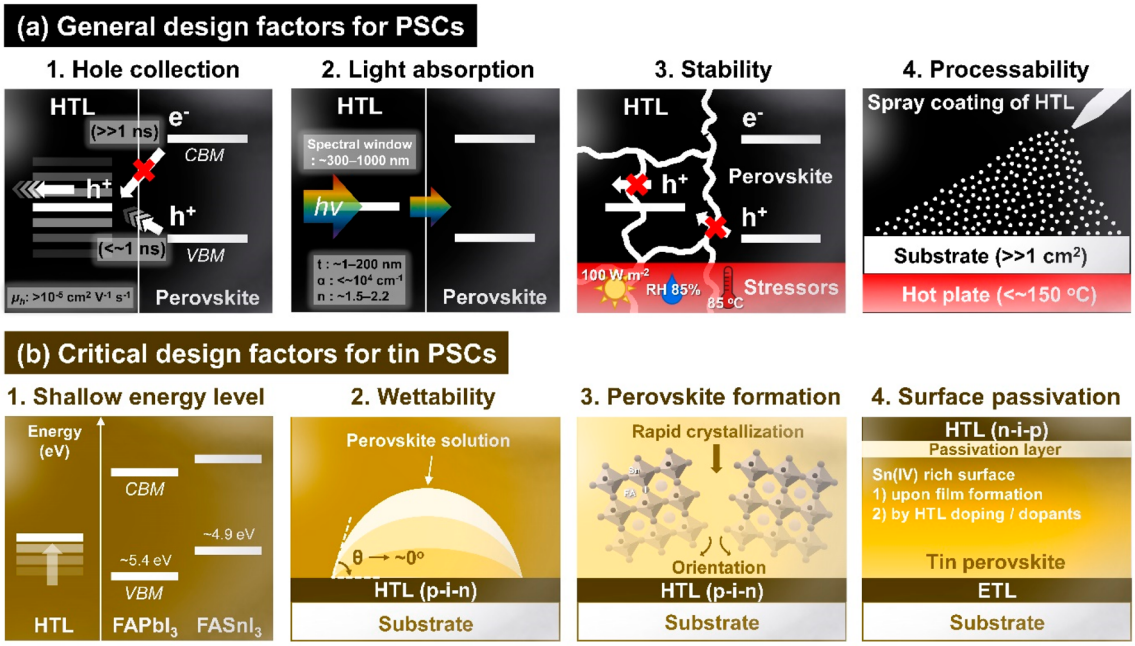

Figure 3. Schematic illustrations showing (a) general HTL design factors for PSCs and (b) critical HTL design factors for tin PSCs.

internal stressors, including ion migration, electric field, and mismatch in volume expansion with perovskites. A variety of techniques based on solution, vapor, and vacuum processing are available for depositing HTLs. The deployment of these techniques should proceed in consideration of film formability and reproducibility, process affordability and up-scalability, and low-temperature processability for broad utility and commercialization of PSCs.[3] The four design factors are intercorrelated and hence should be considered as a whole in designing effective HTLs in PSCs. Importantly, they can serve as a basis for the effective design of HTLs in tin PSCs.

CRITICAL HTL DESIGN FACTORS FOR TIN PSCs

We propose four additional design factors specific to tin PSCs, as shown in Figure 3b, on account of the unique properties of tin perovskites. First, tin perovskites have shallower VBM energy levels than their lead counterparts. For example, formamidinium tin tri-iodide $FASnI_3$ is roughly 0.5 eV shallower in a VBM energy level than a lead analog (Figures 1 and 3b). HTLs for tin PSCs should have shallow energy levels accordingly to facilitate hole collection. To enhance device efficiency and stability, tin perovskites have been engineered by involving mixed cations (FA/PEA (phenethylammonium), FA/GA (guanidinium), etc.),[17,22−29] quasi-two-dimension analogs,[30] or mixed halides (e.g., I/Br),[22] which can lower the VBM energy levels by ∼0.2−0.3 eV, as Figure 1 displays. In this regard, rather than energy level alignment, other factors can exert more influence.

Wetting of tin perovskite precursor solutions on HTL surfaces is essential for p-i-n tin PSCs; otherwise, the resulting films can embed apparent crystal defects epitomized by pinholes or voids due to dewetting. While dimethyl sulfoxide (DMSO) is employed ubiquitously in the precursor solutions, its large surface energy renders relatively poor contact with the hydrophobic (or less hydrophilic) HTLs. This issue is accentuated by rapid crystallization of tin perovskites leading to the disordered orientation of tin perovskite crystals, hence poor contact with the hydrophobic HTLs, possibly resulting in voids between the HTL and perovskite layers.[22] While the above two factors on the solution wettability and perovskite film formability are influential to p-i-n tin PSCs, the last critical factor related to Sn(IV) species can be more influential to n-i-p devices. It is reported that Sn(IV) is populated more on top surfaces, than in bulk, of tin perovskites upon film formation.[31] Oxidative HTL dopants and/or doping processes (e.g., air doping) can increase the population of Sn(IV) atop tin perovskites.[32] The formation of Sn(IV) species gives rise to subsequent Sn vacancy defects whose energy states are likely located around VBM,[1] which would deteriorate hole collection at the top electrode.

> Unlike lead perovskites, tin perovskites are subjected to rapid crystallization and easy oxidation from Sn(II) to Sn(IV), resulting in uncontrollable polycrystalline grain size and orientation as well as a large number of trap states, detrimental to device performance and stability. Therefore, designing effective HTLs for tin PSCs goes beyond the primary consideration of energy level alignment.

RESEARCH PROGRESS ON PEDOT:PSS FOR TIN PSCs

PEDOT:PSS is a polymeric HTL with a hole mobility of 0.045 $cm^2\ V^{-1}\ s^{-1}$. PEDOT:PSS forms a thin film comprised of core−shell (PEDOT−PSS) structures in a network where partially oxidized PEDOT conducts holes while PSS is added to dope PEDOT, adjusts work function, and enables aqueous solution-processing.[5] A thin layer of PSS caps the PEDOT:PSS film. Thus, the hydrophilic surface of PEDOT:PSS allows the

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wetting of the precursor solutions to give rise to high-quality tin perovskite thin films. Additionally, PEDOT:PSS is commercially available (Clevios AI 4083) and can be processed under ambient conditions with high reproducibility. These merits propel the use of PEDOT:PSS HTLs in tin PSCs with a p-i-n architecture.

However, weak HTL properties of PEDOT:PSS are identified on the basis of general design factors such as hole collection and stability. Interfacial defects, ohmic losses in hole transport, and hole transfer barriers add impediments to hole collection by PEDOT:PSS. Adjusting work function can improve energy level alignment for hole transfer.[33] Interfacial defect passivation by forming a SAM,[34] low-dimensional perovskite,[35] diammonium acetates,[36] or potassium thiocyanate[37] on PEDOT:PSS can retard hole recombination.

The stability of PEDOT:PSS remains a great concern for tin PSCs. PEDOT:PSS is strongly acidic due to PSS. Even though PSS is beneficial in suppressing the easy tin disproportionation (Sn(II) → Sn(IV) + Sn(0)) according to the Frost diagram,[38] it is readily moisturized in air due to hygroscopicity, which is detrimental to the long-term stability of both PEDOT:PSS and tin perovskites.[1,39] In this regard, PEDOT:PSS was passivated by a hydrophobic overlayer like poly(methyl methacrylate).[40] Also, PSS-free PEDOT (Clevios HTL Solar 3) was applied.[41]

RESEARCH PROGRESS ON OTHER HTLS FOR TIN PSCs

In addition to PEDOT:PSS, several other organic HTLs such as small molecules (e.g., Spiro-OMeTAD), polymers (e.g., PTAA), and SAMs (e.g., MeO-2PACz), along with inorganic HTLs such as NiO_x, exhibit promising HTL characteristics, despite their somewhat lower performance in tin PSCs. Organic HTLs can benefit from high molecular designability and a rich library while inorganic HTLs offer excellent thermal stability and large areas of contact with perovskites particularly in mesoporous platforms. Moreover, the other HTLs are mostly less hydrophilic than PEDOT:PSS with expectations for prolonged operational stability. Meanwhile, except for NiO_x, other HTLs including Spiro-OMeTAD, PTAA, and MeO-2PACz are explored in tin PSCs by an n-i-p architecture. Uplifting low V_{OC} and FF beyond ∼0.7 V and ∼70.0% to compete with and ultimately excel PEDOT:PSS remains a challenge. The photovoltaic parameters are summarized in the Supporting Information. Nonetheless, HTLs other than PEDOT:PSS are now at a pathfinding stage in tin PSCs.

> In addition to PEDOT:PSS, several other organic HTLs, along with inorganic HTLs, exhibit promising characteristics, despite their somewhat lower performance in tin perovskite solar cells.

Spiro-OMeTAD is a small molecular HTL with triarylamine moieties terminated with methoxy groups (Figure 2a). It requires dopants due to its low hole mobility (∼10^{-4} cm^2 V^{-1} s^{-1}) and large film thickness (∼200 nm) in n-i-p tin PSCs.[42] A conventional dopant material of lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) is deliquescent and necessitates oxygen exposure, hence being detrimental to tin perovskites through Sn(II) oxidation. Therefore, the early-stage efforts on Spiro-OMeTAD failed to achieve satisfactory PCE and stability in tin PSCs. Very recently, an alternative dopant of 4-isopropyl-4′-methyldiphenyliodonium tetrakis(pentafluorophenyl)borate (TPFB), being capable of suppressing Sn(II) oxidation while not needing air doping, was introduced to Spiro-OMeTAD for tin PSCs. It resulted in impressive PCE (10.9%) and unprecedented stability (T_{95} for 2600 h even at a temperature of 85 °C in a glovebox without encapsulation).[32] Despite this, $J-V$ hysteresis and relatively low V_{OC} (<0.7 V) remain unaddressed.[32]

PTAA is a polymeric HTL with a triarylamine-based repeating unit (Figure 2a). Similar to Spiro-OMeTAD, it has low hole mobility of (3−6) × 10^{-4} cm^2 V^{-1} s^{-1} [5] and requires dopants as used in n-i-p devices. The efficient dopant of TPFB is also applicable to PTAA.[43] When coupled with perovskite post-treatment with 2-thiophenemethylammonium iodine, the PCE exceeds 9%.[44] ETL replacement from TiO_2 to Nb_2O_5 leads to a PCE rise to 7.0% from 3.8%.[45] The low V_{OC} (<0.55 V)[44,45] and $J-V$ hysteresis[44] are however accompanied. One publication is available to date on a p-i-n device where PTAA serves as a compact film as thin as <∼10 nm. It thus does not involve dopants but gives rise to an issue of precursor solution dewetting because of the hydrophobicity of PTAA and the polarity of the solvent. Treating PTAA with perovskite precursor salts and adopting two-step perovskite deposition have been excelled to mitigate this challenge.[46] As a result, the PCE of 8.5% and >2-fold higher moisture resistance (at ∼50% RH) than PEDOT:PSS were reported.[46]

Unlike small molecular and polymeric HTLs that are typically several tens of nanometers in thickness, SAM HTLs are monolayers or a few layers of molecules. SAM molecules are comprised of three different groups: a functional group that has p-type moieties with or without dangling moieties (e.g., $-CH_3$, $-OCH_3$, or −Br) to modulate the HOMO levels and the wettability of perovskite precursor solutions, an anchoring group that chemically binds to the surface of transparent conductive oxides (e.g., indium tin oxide, ITO), and a spacer group that adjusts the distance between functional and anchoring groups to vary the interactions between SAM molecules during the self-assembly process and ultimately the SAM quality.[5,47,48] Therefore, SAM HTLs offer the following unique advantages: high resistance to overlay processing because of the stable chemical bonding between the anchoring group and the substrate surface; nearly omitting the hole transport process and suppressing a parasitic light absorption loss because of a monolayer of molecules (in ideal cases); and rich molecular design potential because three functional groups can be varied. With SAM HTLs, the energy level alignment could be less influential to hole transfer, because holes might tunnel through the thin layers. For example, both 2PACz and MeO-2PACz SAMs attain similar PCE in lead PSCs,[9,10] even though their HOMO levels differ by ∼0.5 eV (Figure 1). Despite the great promise, only two publications on SAMs are available in p-i-n tin PSCs.[49,50] One publication is on MeO-2PACz which consists of a carbazole functional group known for good hole selectivity with dangling methoxy moieties for wettability, phosphonic acid as an anchoring group for strong binding onto an ITO surface, and an ethyl spacer group for a high-quality SAM, as Figure 2a shows.[47] MeO-2PACz has a proper HOMO level (−5.1 eV, Figure 1) and forms a fairly hydrophilic surface due to the methoxy moieties among analogous SAMs.[50] Following substrate preconditioning, MeO-2PACz was successfully implemented with excellent wettability to the precursor solution.[50] The resulting devices attained

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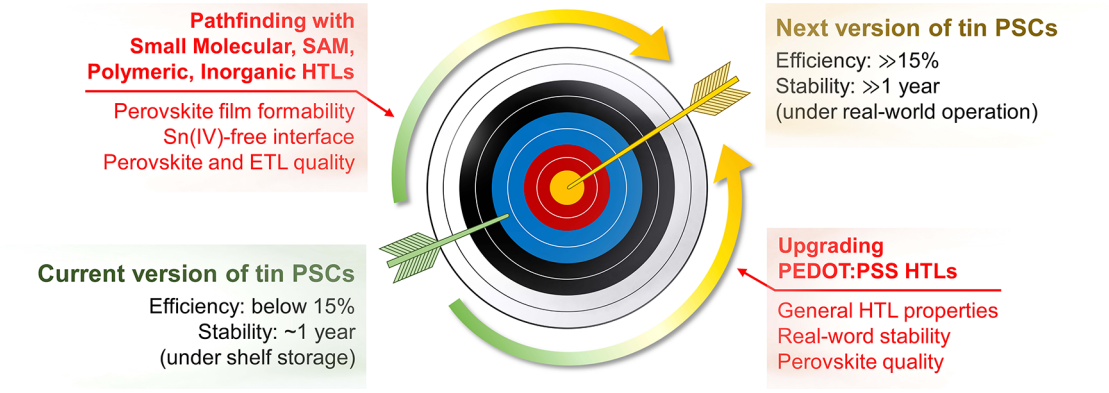

Figure 4. A sketch exhibiting the proposed HTL research direction to leap to the next level of tin PSCs.

inspiring performance with PCE of 6.5% and a shelf-storage lifetime of 1900 h for T_{80}.[50] The other publication is on newly designed and synthesized SAM molecules, which have X-shaped quinoxaline as an electron-withdrawing core moiety in a spacer group, two anchoring groups of −CN/−CN or −CN/−COOH that are conjugated with phenyl rings or thiophene units, and triphenylamine-based functional groups.[49] Even though these X-shaped SAM molecules are comparable to MeO-2PACz in terms of the precursor solution wettability and HOMO level (∼−5.1 eV), they are distinct by having fully conjugated structures to facilitate charge transfer and thiophene moieties to promote better quality tin perovskites. These merits yield PCE of 8.3% and a shelf-storage lifetime of >1600 h for T_{90}.[49]

NiO_x is an inorganic HTL with hole mobility of >0.1 cm^2 V^{-1} s^{-1} without the need of dopants. It has a cubic crystal structure with a space group *Fm*3*m* and a lattice parameter of 0.4173 nm. The surface of NiO_x is nonstoichiometric with NiOOH, Ni_2O_3, and $Ni^{\geq 3+}$ species.[6,11,51] NiO_x takes the second place of 13.79% PCE with a p-i-n device architecture and ICBA as an ETL on account of high V_{OC} exceeding 1 V.[52] NiO_x has also been used in n-i-p devices with PCE of below 10%.[53] Remarkable ambient air stability of 1000 h for $T_{\sim 80}$ with RH 20% for unencapsulated devices[54] and 1680 h for $T_{>100}$ under an N_2 environment[55] were reported. The unencapsulated devices with Cu-NiO_x HTLs achieved efficiency of 10.9% and stability of 500 h for T_{77} in N_2 atmosphere at 40 °C.[56] NiO_x has not yet been adopted widely as a HTL in tin PSCs to our knowledge, which is likely because $Ni^{\geq 3+}$ surface species are reactive to perovskite components,[11] exemplified by Sn(II) oxidation at the interface with tin perovskites. In light of this, surface protection using thin films of benign metal oxides like GeO_2 can be a fascinating option.[57] Owing to the protection, an extended device lifetime under maximum power point tracking with 1 sun illumination in N_2 atmosphere at ∼45 °C was recorded to be 700 h for T_{80} in contrast to 123 h for T_{50} for pristine NiO_x and 700 h for T_{53} for PEDOT:PSS.[57]

Several organic HTLs have been explored in n-i-p tin PSCs. A small molecule, composed of one tetraphenylethene core with four end-capped triphenylamine units and named as TPE, was synthesized with cost efficiency.[52] With no dopants, the TPE HTL enables higher PCE of 7.02% than 5.20 and 6.67% for the doped Spiro-OMeTAD and PTAA HTLs respectively, alongside minimal hysteresis of *J*−*V* curves and ∼2−5-fold better ambient stability.[52] Another version of small molecules based on 4,8-di(thiophen-2-yl)benzo[1,2-*b*:4,5-*b*′]dithiophene (BDT) as a central unit with di- and tetra-4,4′-dimethoxy-triphenylamine substituents were synthesized.[58] These BDT-based HTLs have a HOMO level of ∼−5.0 eV and hole mobility >10^{-3} cm^2 V^{-1} s^{-1}. As the efficient dopant of TPFB is incorporated to these HTLs, 7.59% PCE, minimal hysteresis of *J*−*V* curves, and a long shelf-storage lifetime of ∼14 months for $T_{66.9}$ in an N_2-filled glovebox were attained.[58] The well-known hydrophobic polymeric HTL of poly(3-hexylthiophene) (P3HT) was also explored.[59] In addition to 7.5% PCE and insignificant *J*−*V* hysteresis, the P3HT HTLs showcased an inert shelf-storage lifetime of 1440 h for $T_{60.2}$ and an ambient lifetime of 120 h for $T_{76.5}$, respectively.[59] In common, the TPE, BDT, and P3HT HTLs are subjected to V_{OC} below 0.5 V regardless of the distinct bandgaps of the used tin perovskites.[52,58,59]

In p-i-n devices, several organic and inorganic HTLs have been explored. Pyrrolopyrrole-based polymer HTLs incorporating three thioalkylated bithiophene and long alkyl chains were synthesized.[60] Pyrrolopyrrole is electron-donating to push HOMO levels up to −5.00 to −5.07 eV and can be tailored with various functional groups. Moreover, the other units in the polymer enhance the π-conjugation via forming an intramolecular S(alkyl)···S(thiophene) lock.[60] The collective chemical functions make pyrrolopyrrole-based polymers excellent HTLs.[60] These HTLs require preconditioning with anilinium iodide for wetting the perovskite solution.[60] Nonetheless, these HTLs attained remarkable shelf-storage stability (>6000 h) in an N_2-filled glovebox without encapsulation, along with 7.6% PCE.[60] As inorganic HTLs, MoO_3[61] and CuSCN[62] were implemented in tin PSCs. The respective PCE values were measured to be 0.55% and 7.34%. The encapsulated devices with CuSCN HTLs led to ambient stability of 10 h for $T_{>60}$ and RH 20% and shelf-storage stability of >1000 h for T_{70} in an N_2-filled glovebox. Recently, a new type of an inorganic HTL of SnO_x was reported which can be prepared by treating tin metal with plasma.[63] Using this SnO_x HTL, tin PSCs demonstrated high PCE of 14.09% and stability of 50 days for T_{100} in an N_2 atmosphere.[63]

PERSPECTIVE ON PEDOT:PSS AND OTHER HTLs

The current best tin PSCs, with PEDOT:PSS, exhibit PCE of 14.81% resulting from V_{OC} of 0.84 V, short-circuit current density (J_{SC}) of 24.91 mA cm^{-2}, and FF of 70.76%.[17] In comparison, the best lead-based counterparts, with Spiro-OMeTAD, have 26.08% PCE, resulting from V_{OC} of 1.178 V, J_{SC} of 25.69 mA cm^{-2}, and FF of 86.15%.[7] The prominent dissimilarity stems from V_{OC} and FF. According to the

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Shockley−Queisser limit, tin perovskites can have a bandgap of 1.4 eV to enable J_{SC} to reach 32.91 mA cm^{-2} whereas that of lead perovskites is larger by approximately 0.1 eV for 28.97 mA cm^{-2}.[64] In this regard, a relatively large J_{SC} deficit is identified in tin PSCs. Overall, all photovoltaic parameters are significantly lower with tin PSCs. The origins to account for this can arise from imperfect HTL interfacial properties and tin perovskite quality and thickness (∼200 nm). Meanwhile, the best stable tin PSC, with PEDOT:PSS, attains a 1 year lifetime under N_2 shelf-storage.[18] Few reports show promising device stability under harsh conditions for real-world operations. Taken together, in pursuit of overcoming the efficiency and stability limits, we outline two prospective research directions with emphasis on HTLs for tin PSCs: 1) upgrading PEDOT:PSS and 2) pathfinding with other organic and inorganic HTLs, sketched in Figure 4.

Despite the earlier attempts to modify PEDOT:PSS, the high-performance tin PSCs are achieved by using pristine PEDOT:PSS as a HTL. In this regard, more studies can be devoted to modifying and, thus, upgrading PEDOT:PSS for tin PSCs. Dedoping PEDOT and reducing film thickness can minimize the absorption loss.[65] The low hole mobility can be improved by additive engineering or post-treatment to alter the physical and chemical structure of PEDOT and/or reduce the insulating PSS.[66,67] The reduction of PSS can uplift the HOMO energy level to be better suited to tin perovskites.[34] The PEDOT:PSS interfacial defects which are detrimental to hole collection can be suppressed by passivation.[36] Other strategies such as varying PEDOT:PSS weight ratios,[68] functional groups to PEDOT,[67,69] and using different molecular weight PSS[70] can also be considered to improve device performance and stability.

Taken together, in pursuit of overcoming the efficiency and stability limits, we outline two prospective research directions with emphasis on hole transport layers for tin perovskite solar cells: 1) upgrading PEDOT:PSS and 2) pathfinding with other organic and inorganic HTLs.

Other organic and inorganic HTLs are now at a pathfinding stage in n-i-p and p-i-n tin PSCs. Their maximal PCE has seemingly not yet been unlocked, staying at ∼10% or below due largely to V_{OC} < ∼0.7 V and FF < ∼70.0%. The device stability is progressed to a limited extent. For example, the N_2 shelf-storage lifetime mostly reported is below ∼2000 h for $T_{\geq 80}$. For detailed information, the photovoltaic parameters for these HTLs are summarized in the Supporting Information.

In p-i-n devices, the formation of tin perovskite films of high quality onto polymers, SAMs, or analogs could become very demanding, associated with hydrophobicity and interactivity (e.g., hydrogen bonding). The same issue often comes up for lead counterparts, but it appears to be vastly problematic for tin PSCs due to rapid crystallization. As a universal approach, depositing an overlay of complementary properties (i.e., demanding surface energy and interaction with perovskite components) to existing HTLs such as PTAA, P3HT, and MeO-2PACz can be simple yet effective. Polymers, or others with high resistance to the perovskite solution process in p-i-n devices, could serve as an effective overlay. One such example is poly(9,9-bis(3′-(*N*,*N*-dimethyl)-*N*-ethylammonium-propyl-2,7-fluorene)-*alt*-2,7-(9,9-dioctylfluorene))dibromide (PFN-Br) which is amphiphilic by a hydrophobic backbone and hydrophilic ionic functional groups to be interactive with both HTL and perovskite. The thickness and morphology of overlayers should be sophistically controlled, since they could affect the hole transfer. Moreover, it is desired that the overlayer can reduce interfacial defects and suppress tin oxidation. In this regard, the reductive moieties such as urea, amine, hydrazine, and carboxylic acid could be integrated into organic molecules and polymers to serve as overlayers.

In the design of organic HTLs beyond introducing overlays, tailoring end groups with polar, acid, and/or alkyl moieties can be considered. Relevant lessons can be learned from precedents regarding lead PSCs. The dendritic small-molecular HTLs are constructed with the diphenylamine and carbazole groups for excellent hole transport and the peripheral methoxy groups for interface passivation and perovskite film formability.[71] For SAM molecules, adding a cyanovinyl moiety can enable SAM HTLs with highly wettable surfaces.[72] Other terminal groups such as −CN, $-NH_2$, $-NO_2$, −COOH, and −F can tune the water contact angles of SAM surfaces widely in the range of ∼30°−130°.[47] Including the aforementioned reductive moieties to SAM molecules needs to be taken into account. We need to note that leveraging the high molecular designability of organic materials can enable fine-tuning of the HTL properties to be well-suited to tin PSCs.

For inorganic HTLs, porosity and surface roughness play crucial roles by providing substantial contact areas with perovskite layers. This can be advantageous in terms of improved wettability and enhanced interface contact, according to the Wenzel model.[73] For instance, if mesoporous NiO_x is modified by hydrophilic methoxy-based SAMs or post-treated with perovskite cations like FAI and PEAI, the wettability could be enhanced, which, in turn, could improve the film formability of perovskite layers and bolster the stability of interface.

In n-i-p devices, the use of low-temperature-processable small-molecular and polymeric HTLs such as Spiro-OMeTAD and PTAA can still be advantageous, provided they are appropriately doped. Exploring other polymeric HTLs, including P3HT, holds potential as well. The principal aim of HTLs in n-i-p devices is to passivate and eventually eliminate Sn(IV) defects on the top surfaces of tin perovskites. A viable strategy involves addressing and stabilizing these defects before depositing the HTLs. Given the relatively thick HTL films (∼100 nm) in n-i-p devices, there is a continuous pursuit to identify benign dopants. Ideally, these dopants should possess the capability to stabilize Sn(II). As alternatives free from dopants, inorganic HTLs like NiO_x emerge as appealing choices due to their high hole mobility. NiO_x can be conformally deposited through methods like atomic layer deposition,[11] which minimally affects the top surface of perovskite. Moreover, operational stability can benefit from HTLs with hydrophobic properties.

Before we draw final conclusions, it is crucial to emphasize several overlooked aspects. In the development of HTL materials, methods, and strategies, researchers must consider potential accompanying effects on the design factors presented in Figure 3. Moreover, these designs should evolve to encompass a comprehensive view at the device level. In

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pursuing this goal, the development of novel HTLs should invite concurrent development of perovskites and ETLs. This holistic approach is pivotal for achieving balanced charge transport, as well as for reducing charge accumulation and recombination.[5]

The VBM of tin perovskite is notably responsive to changes in chemical composition and the presence of mixed cations and/or halides (e.g., FA/PEA and/or I/Br).[22] The inhomogeneous distribution across tin perovskite films could result in variations in the VBM energy levels at the top and bottom. The methods used to measure energy levels (e.g., ultraviolet photoelectron spectroscopy or scanning Kelvin probe microscopy) scan the top surfaces in most cases. Measuring the practical VBM energy levels of buried tin perovskites that are in contact with HTLs in p-i-n devices becomes challenging unless the top and bulk films are appropriately etched.

Gaining a comprehensive understanding of the distribution of Sn(IV) defects across the entire cross sections of tin perovskite layers could be instructive in designing effective HTLs not only in p-i-n devices but also in n-i-p devices. Specifically, just as Sn(IV) defects can be present on the top surfaces and within the bulk, the bottom interfaces of tin perovskites with HTLs could contain Sn(IV) defects. Since the ITO or fluorine-doped tin oxide substrates have Sn(IV) species and are closely positioned to HTLs, a careful evaluation of tin elements is essential. This analysis is crucial for making informed decisions in assessing the impact of these defects on device performance and for optimizing the design of HTLs.

Recent progress in p-i-n devices, particular those involving less hydrophilic or hydrophobic HTLs such as SAMs,[49,50] PTAA,[46] and other polymers,[60] has primarily been achieved through the fabrication of tin perovskites using pure DMSO-based precursor solutions and the two-step deposition method. However, significant potential for advancement remains through the exploration of solvent engineering and alternative deposition methods for tin perovskite layers coupled with concurrent HTL development. Investigating the interlayer between solvent engineering techniques and deposition methods for tin perovskites while simultaneously optimizing HTL materials could yield promising avenues for further enhancement in device performance.

Similar to their lead-based counterparts, hydrophobic HTL surfaces offer a means to manipulate the quality of tin perovskites. For example, hydrophobic HTLs can reduce the density of nuclei, resulting in larger crystals and/or thicker films.[74] Consequently, as control over the rapid crystallization process becomes more attainable, this could open up new avenues for enhanced light harvesting on account of the formation of higher quality tin perovskites, as well as the improved hole collection facilitated by the HTLs. These combined effects may contribute to substantial advancement of the overall performance of tin PSCs.

CONCLUSIONS AND OUTLOOK

Tin PSCs present two prominent advantages: reduced toxicity compared to their lead counterparts and the potential for higher theoretical efficiency. We foresee that these attributes position tin PSCs as promising candidates for niche applications, including bioelectronics, wearable devices, and building-integrated photovoltaics for enhanced safety measures. In this context, a strategic focus on improving HTLs through advancements in materials such as upgrading PEDOT:PSS and developing novel alternatives can not only elevate the efficiency and stability of tin PSCs to compete with lead-based counterparts but also facilitate their integration into niche applications. Furthermore, well-designed HTLs can have broader implications, extending to various photovoltaic and optoelectronic applications. Hence, the proposed design strategies articulated in this Perspective can stimulate fundamental investigations, which, in turn, can lead to the development of effective HTLs and transformative technologies for sustainable photovoltaics and optoelectronics.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsenergylett.3c01410.

Summary of energy level and device performance (XLSX)

AUTHOR INFORMATION

Corresponding Author

Qiuming Yu − *Robert Frederick Smith School of Chemical and Biomolecular Engineering, Cornell University, Ithaca, New York 14853, United States;* orcid.org/0000-0002-2401-4664; Email: qy10@cornell.edu

Authors

Donghoon Song − *Robert Frederick Smith School of Chemical and Biomolecular Engineering, Cornell University, Ithaca, New York 14853, United States;* orcid.org/0000-0003-0914-1507

Shripathi Ramakrishnan − *Robert Frederick Smith School of Chemical and Biomolecular Engineering, Cornell University, Ithaca, New York 14853, United States*

Yuanze Xu − *Robert Frederick Smith School of Chemical and Biomolecular Engineering, Cornell University, Ithaca, New York 14853, United States;* orcid.org/0000-0002-4873-6629

Complete contact information is available at: https://pubs.acs.org/10.1021/acsenergylett.3c01410

Author Contributions

All authors contributed to proposing the concept of the manuscript. D.S. drafted the manuscript and prepared figures and the Excel file with the help of S.R. and Y.X. D.S. and Q.Y. edited the manuscript while S.R. and Y.X. provided comments and additional edits. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

Biographies

Donghoon Song received his Ph.D. at Hanyang University, Seoul, and is a postdoctoral research associate at Cornell University, Ithaca, New York. His research interests include lead-free tin perovskites, perovskite and dye-sensitized solar cells, printed electronics, and probing material−structure−device relationships.

Shripathi Ramakrishnan received his M.S. in Chemical Engineering from the University of Washington in 2020. He is now a Ph.D. student in the lab of Prof. Qiuming Yu at Cornell University. His research interests include the formation dynamics, photophysics, and structure−property relationships of 2D perovskites for implementation in solar cells.

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Yuanze Xu received his M.S. in Chemical and Biomolecular Engineering at Cornell University and continued to pursue his Ph.D. degree in Prof. Qiuming Yu's lab. His research interests include lead-free perovskite solar cells, perovskite quantum dots, and ultrafast spectroscopy.

Qiuming Yu received her Ph.D. in Chemical Engineering from Cornell University in 1995. She joined the School of Chemical and Biomolecular Engineering at Cornell University in July 2020 as a professor. Her research interests include the fundamental studies of plasmonic and semiconductor materials and their biosensing and optoelectronic applications.

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