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Multifunctional organic ammonium salt-modified SnO₂ nanoparticles toward efficient and stable planar perovskite solar cells⁺

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Bulk and interfacial nonradiative recombination hinder the further enhancement of the power conversion efficiency (PCE) and stability of SnO₂-based planar perovskite solar cells (PSCs). To date, it is still a huge challenge to minimize the bulk and interfacial nonradiative recombination losses, and thus maximize the potentials of PCE and stability. Herein, a novel and effective multifunctional modification strategy through incorporating Girard's Reagent T (GRT) molecules with multiple functional groups to modify SnO₂ nanoparticles (NPs), which significantly reduces the bulk and interfacial nonradiative recombination losses through the simultaneous achievement of suppressing nanoparticle agglomeration, improving the electronic property of SnO₂ films, facilitating the vertical growth and enlarging the grain size of perovskite crystals, and passivating interfacial defects is reported. As a result, the device based on GRT modification delivers a much higher PCE of 21.63%, along with significantly suppressed hysteresis, as compared to the control device (19.77%). The device stability is ameliorated after GRT modification. The unencapsulated device with GRT maintains 99.5% of its initial PCE after aging at 60 °C for 720 h and 58.5% after illumination for 672 h under one sun. respectively. The present work provides guidance for the design of multifunctional modification molecules toward efficient and stable PSCs.

Introduction

Since the first report on all-solid-state perovskite solar cells (PSCs),¹ extremely rapid development in the past few years has been experienced.²⁻⁶ The continuous improvement of the power conversion efficiency (PCE) enables PSCs to compete with silicon-based photovoltaics, which currently dominate the photovoltaic market. To date, a record-certified PCE as high as 25.5% has been achieved, which is approaching a PCE value of 26.1% for single crystal silicon solar cells.7 Although great achievements have been made, there is huge room in PCE enhancement, considering the theoretical Shockley-Queisser limit efficiency over 30% for single-junction PSCs.8 Moreover, the current poor operational stability of PSCs hinders its largescale commercial application. It has been extensively demonstrated that the bulk and interfacial nonradiative recombination should be mainly responsible for PCE and stability losses.8,9 Consequently, it is highly desirable to further improve both PCE and stability through maximizing the bulk and interfacial nonradiative recombination losses.

Compared with mesoporous TiO2-based PSCs, SnO2-based PSCs have received increasing attention due to its lowtemperature fabrication, low hysteresis, and excellent ultraviolet (UV) stability.6,10-13 SnO2 films can be fabricated by different approaches, such as sol-gel method,14 chemical bath deposition,15,16 quantum dot,17 and commercial nanoparticles (NPs).10,13 Presently, much higher PCEs have been demonstrated in PSCs based on commercial SnO₂ NPs as compared to other approaches.^{10,12} However, PSCs prepared by commercial SnO₂ NPs usually suffer from poor reproducibility due to the easy nanoparticle agglomeration, which always perplexes researchers and impedes its further development.12,18-20 In past several years, some molecules (e.g., ethylene diamine tetraacetic acid (EDTA),¹⁸ NH₄Cl,²⁰ heparin potassium,¹² polyethylene glycol¹⁹) have been developed to modify commercial SnO₂ NPs, which led to improved PCE and stability, as well as reproducibility. Above results strongly indicate that it is a feasible and effective approach to improve the electronic properties of SnO₂

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NP electron transport layers (ETLs) and the reproducibility of corresponding devices *via* developing appropriate molecules to modify SnO_2 NPs. Therefore, it is urgently needed to design and develop more efficient molecules to modify SnO_2 NPs for the purpose of further enhancement of the efficiency and stability.

Except for SnO₂ ETL, the quality of perovskite films plays a critical role in achieving efficient and stable PSCs. To date, various strategies have been adopted to modulate perovskite crystallization and thus improve its quality, such as composiengineering,21,22 additive engineering,23-25 tion stoichiometric engineering,²⁶ dimensionality engineering,²⁷ precursor and antisolvent engineering,28,29 and perovskite growth substrate engineering.13 Among these, perovskite growth substrate engineering has been certified to be one very effective method for modulating perovskite crystallization.12,13,30,31 Apart from the regulation of perovskite crystallization, defects at the SnO₂/perovskite interface from either the surface of SnO₂ or the surface of the perovskite films are closely related to the stability, PCE and hysteresis of the SnO₂-based PSCs. Some interfacial molecules have been developed to passivate defects at the SnO₂/perovskite interface without improving the perovskite morphology.^{27,32} It is worth noting that some interfacial modifiers have been developed to modify the SnO₂/perovskite interface, resulting in the simultaneous realization of improving the perovskite crystallization and passivating the interfacial defects/trap states.13,33 However, it is still a big challenge to enhance the electronic properties of SnO₂ NPs, passivate interfacial defects, and improve perovskite crystallization simultaneously only through a simple and effective strategy. Interestingly, You et al. improved the quality of the SnO₂ films and perovskite films, as well as the interfacial contact, leading to an enhancement in the PCE and stability.12 This work suggests that it is feasible and effective to improve the electronic properties of the SnO2 NPs, passivate the interfacial defects, and improve the perovskite crystallization simultaneously via incorporating a proper multifunctional modification molecule into the SnO₂ film. Consequently, further improvement of the stability and PCE of the SnO2 NP-based PSCs is highly expected by rationally designing and developing more efficient multifunctional modifiers.

In the present work, we have developed a novel multifunctional modification strategy, where a bio-hormone extractant named as Girard's Reagent T (GRT) is incorporated into the SnO₂ NP colloidal solution, resulting in the simultaneous achievement of suppressing nanoparticle agglomeration, improving the electronic property of the SnO₂ films, facilitating the vertical growth and enlarging the grain size of the perovskite crystals, and passivating interfacial defects. The multiple different kinds of functional groups in the GRT molecules enable the realization of the above multiple functions. As a result, the PCE is increased from 19.77% to 21.63% after GRT modification, which is mainly a result of the significantly improved open-circuit voltage (V_{OC}) , along with slightly enhanced short-circuit current density (J_{SC}) and fill factor (FF). The unencapsulated device with GRT maintains 99.5% of its initial PCE after aging at 60 °C for 720 h, and 58.5% after aging for 672 h under one sun illumination, respectively. Improved

charge extraction, charge transport, and suppressed bulk and interfacial nonradiative recombination should be responsible for the above improved PCE and stability.

Results and discussion

In order to further improve the PCE and stability of the SnO₂based PSCs, we designed and incorporated GRT molecules to modify the SnO₂ NPs. The effect of GRT modification on the dispersion of SnO₂ NPs, perovskite film growth, and interface between the SnO₂ ETL and perovskite film is schematically illustrated in Fig. 1a. Since GRT molecules contain several different kinds of functional groups, it is expected to achieve multiple functions by the modification of GRT for SnO₂ NPs. First, the carbonyl group is expected to be able to block the agglomeration of SnO₂ NPs, promote their uniform dispersion and passivate oxygen vacancy defects from SnO₂ through bonding to the surface of the SnO₂ NPs via the coordination reaction between -C=O and Sn⁴⁺. Second, the quaternary ammonium chloride salt is anticipated to facilitate the crystal growth of perovskites, and thus improve the perovskite film quality. It was reported in our previous work that the incorporation of organic ammonium salts at the ETL/perovskite interface can improve the quality of the perovskite films by facilitating the perovskite crystal growth.13 Third, it is anticipated that the quaternary ammonium cation and chloride anion could passivate anionic defects (e.g., Pb-I antisite defects and formamidinium (FA⁺) or methylammonium (MA⁺) vacancies) and cationic defects (e.g., undercoordinated Pb) at the ETL/ perovskite interface. Organic or inorganic salts as interfacial modifiers13,32,34,35 or additives24,25 have been extensively demonstrated to be capable of passivating anionic and cationic defects. In addition, it was widely revealed that Cl⁻ can effectively increase the carrier lifetimes, carrier diffusion length, and passivate the grain boundary (GB) defects.³⁶⁻³⁸ Finally, the hydrazine functional group in the GRT molecules is expected to be able to improve the SnO2 NP dispersion and interfacial contact between ETL and the perovskite layer via formation of hydrogen bonds either with -OH at the surface of the SnO2 NPs or cations from perovskites. All in all, multiple functions are anticipated to be achieved through the modification of the GRT molecules for SnO₂ NPs.

As expected, the chemical interaction between the GRT molecules and SnO₂ NPs was observed from the photographs of the deionized water solutions with GRT, SnO₂ NPs, and SnO₂ NPs modified by GRT (Fig. 1b). Obviously, both SnO₂ and GRT solutions were transparent, while the SnO₂ solution with GRT was cloudy milky white, which indicates that a strong chemical interaction probably existed between GRT and the SnO₂ NPs. Fourier-transform infrared (FTIR) and X-ray photoelectron spectroscopy (XPS) were performed to further study the chemical interaction between GRT and SnO₂. As shown in Fig. 1c and S1,† the characteristic peak at 1689 cm⁻¹ of -C=O in GRT¹² was shifted to a lower wavenumber of 1679 cm⁻¹ after the modification of GRT for SnO₂. Moreover, the peak of Sn–O–Sn was shifted from in the SnO₂ film to GRT-modified SnO₂ film. The above results suggest that the coordination reaction happened



Fig. 1 (a) Schematic diagram of the preparation process of perovskite films deposited on the SnO_2 films without and with GRT modification, which shows that GRT can facilitate the uniform dispersion of SnO_2 NPs, promote the vertical growth of perovskite crystals, and passivate interfacial defects at the SnO_2 /perovskite interface. (b) Photographs of the water solutions with pure GRT, SnO_2 , or $SnO_2 + GRT$. (c) FTIR spectra of GRT and SnO_2 films without and with GRT modification. (d) XPS spectra of SnO_2 films without and with GRT modification. (e) Zeta potential of SnO_2 and SnO_2 modified by GRT. DLS spectra of fresh and aged (f) SnO_2 and (g) SnO_2 with GRT colloidal dispersions.

between -C=O in GRT and SnO₂. The full XPS spectra is presented in Fig. S2a.[†] It was found clearly from Fig. 1d that the binding energies of the Sn $3d_{3/2}$ (494.3 eV) and Sn $3d_{5/2}$ (486.0 eV) peaks of SnO₂ were shifted to higher binding energies of 494.6 and 486.3 eV after GRT modification, respectively, indicating the strong chemical interaction between GRT and SnO₂, which is consistent with the conclusion from FTIR results. In addition, the Cl 2p was found in the GRT modified SnO₂ film, but not in the SnO₂ film (Fig. S2b[†]). In one word, both FTIR and XPS results confirmed the existence of GRT in the final SnO₂ films and the strong chemical interaction between GRT and SnO₂. Zeta potential measurements were conducted to gain insight into the effect of GRT modification on the dispersion of SnO₂ NPs. As shown in Fig. 1e, the increased Zeta potential from 51.14 mV to 63.14 mV after GRT modification suggests that the incorporation of GRT can effectively facilitate the uniform dispersion of SnO₂ NPs by suppressing their agglomeration. Subsequently, dynamic light scattering (DLS) measurements were performed to investigate the effect of GRT modification on the colloidal particle sizes in the fresh solution and aged for 10 days. As exhibited in Fig. 1f, the average colloidal particle size of the bare SnO₂ solution was increased from 48.14 nm to

130.54 nm after aging for 10 days. In contrast, almost identical colloidal particle sizes were found in the fresh GRT modified SnO_2 solution (35.01 nm) and aged for the same time (36.10 nm) (Fig. 1g).

GIXRD measurement was carried out to investigate the effect of GRT modification on the crystallinity and crystal structure of SnO₂ films. As exhibited in Fig. S3,[†] GRT modification was found to not affect the crystal structure of the SnO₂ film. However, the peak intensity of SnO2 modified by GRT was higher than unmodified SnO2, which means that the GRT modification increased the crystallinity of SnO₂ films. The improved crystallinity should be attributed to the suppressed agglomeration. Since the roughness and wettability of the substrates are key to the crystallization and growth of perovskite, we investigated the effect of GRT modification on the roughness and wettability of the SnO₂ films. First, atomic force microscopy (AFM) was measured to reveal the morphology of the SnO₂ films without and with GRT modification. The root mean square (RMS) roughness was reduced from 2.84 nm of the control film to 2.01 nm of the target film with GRT modification (Fig. 2a and b), which is due to the suppressed agglomeration and thus reduced colloidal size resulting from the chemical



Fig. 2 AFM images of (a) SnO_2 and (b) SnO_2 with GRT films spin-coated on the ITO substrates. Contact angle test of water on (c) SnO_2 and (d) $SnO_2 + GRT$ films.

interaction between GRT and SnO2 NPs. This shows that a smoother surface of the SnO₂ film with GRT was obtained, as compared to the reference film. Subsequently, we conducted contact angle measurements to study the effect of GRT modification on the wettability of the SnO₂ films. As revealed in Fig. 2c and d, the contact angle was reduced after GRT modification, which is ascribed to the excellent hydrophilic nature of the GRT molecules. It is inferred that the reduced roughness and improved wettability of the SnO₂ film substrates could be beneficial for the crystallization and growth of perovskites. The electron mobility was slightly increased for the GRT-modified film in comparison with the control film (Fig. S4[†]), which is because of the improved quality of SnO₂ films through suppressing the nanoparticle agglomeration and passivating the possible oxygen vacancy defects. Improved electron mobility will be conducive to the electron transport in SnO₂ films, leading to reduced nonradiative recombination. The above results imply that the GRT-modified SnO₂ is appropriately used as ETL in PSCs.

The reduced roughness, improved wettability, and enhanced electronic property of the SnO₂ film after GRT modification encouraged us to further gain insights into the effect of GRT modification on the quality of perovskite films. The perovskite film based on SnO₂ with GRT showed a slightly improved UV absorption intensity, as compared to the control film (Fig. 3a). As exhibited in Fig. 3b, improved perovskite crystallinity was realized after GRT modification compared to the control perovskite film. The ameliorative crystallinity should be responsible for the increased light harvesting, as discussed above. Fig. S5a and c† present the scanning electron microscopy (SEM) images of the perovskite films deposited on the SnO₂ film and SnO₂ film modified by GRT. The grain size was increased

from 1.21 µm of the control film to 1.52 µm of the target perovskite film based on the GRT modification (Fig. S5b and d[†]). After GRT modification, the roughness of the perovskite films was decreased from 36.97 nm to 21.18 nm (Fig. S6[†]). As revealed by cross-sectional SEM images in Fig. 3c, large holes can be seen in the perovskite film deposited on the unmodified SnO₂ film. The cross section of the control film was formed through the random stack of the unordered perovskite grains. In contrast, the cross section of the perovskite films prepared on GRT-modified SnO₂ was composed of the vertically oriented large grain, which was across the whole cross section (Fig. 3d). Grazing-incidence wide-angle X-ray scattering (GIWAXS) was carried out to further gain insight into the orientation of the perovskite grains. As presented in Fig. S7,† the perovskite film deposited on the SnO₂ + GRT substrate showed brighter scattering rings corresponding to the (101) and (202) planes of the perovskite in comparison with the one deposited on the bare SnO₂ substrate, indicating that the crystallinity and the orientation of the perovskite film were improved after GRT modification, which was in good agreement with the cross-sectional SEM results. Li et al. also demonstrated that the improved crystallinity and the orientation of the perovskite film can be achieved by modifying the SnO2 ETL.12 The improved grain size and crystallization could be attributed to the reduced surface roughness of SnO₂ ETL and improved substrate wettability. In order to further investigate the effect of GRT modification on the perovskite film quality, space charge limited current (SCLC) technology was employed to quantitatively calculate the defect densities of the perovskite films. Fig. 3e and f exhibit the typical dark current-voltage (I-V) curves of the electron-only devices with the structure of ITO/SnO2/perovskite/PCBM/BCP/Ag and ITO/SnO₂ + GRT/perovskite/PCBM/BCP/Ag. Two clear regions



Fig. 3 (a) UV-Vis absorption spectra and (b) XRD patterns of the perovskite films prepared based on SnO_2 films without and with GRT modification. Cross-sectional SEM images of (c) ITO/ SnO_2 /perovskite and (d) ITO/GRT-modified SnO_2 /perovskite samples. The scale bar is 450 nm. Dark *I*-*V* curves of the electron-only devices with the structures of (e) ITO/ SnO_2 /perovskite/PCBM/BCP/Ag and (f) ITO/ SnO_2 + GRT/perovskite/PCBM/BCP/Ag. PL mapping images of the perovskite films prepared on the (g) glass and (h) glass + GRT substrates.

were observed, including the Ohmic region at low bias. This result exhibits a linear correlation between the current and electric field and the trap-filled limited region at the intermediate bias region, which shows a sharp increase in the current. In the trap-filled limited region, the trap density levels are continuously filled, and all of the traps are filled until the trapfilled limit voltage (V_{TFL}).¹³ It is well known that the trap density can be calculated according to the following equation:^{13,23}

$$n_{\rm t} = \frac{2\varepsilon\varepsilon_0 V_{\rm TFL}}{eL^2} \tag{1}$$



Fig. 4 (a) SSPL and (b) TRPL spectra of the perovskite films deposited on non-conductive glass, SnO_2 , and GRT-modified SnO_2 substrates. PL mapping image of the perovskite films prepared on the (c) SnO_2 , and (d) GRT-modified SnO_2 substrates (500 μ m \times 500 μ m). (e) Transient photocurrent and (f) transient photovoltage decay curves of the PSCs based on SnO_2 and GRT-modified SnO_2 GRT ETLs. (g) V_{OC} as a function of light intensities for the devices based on SnO_2 and GRT-modified SnO_2 GRT etc. (g) V_{OC} as a function of GRT modification, which was measured at a bias of 0.8 V in the frequency range of 1 MHz to 0.1 Hz under one sun illumination.

where ε_0 is the vacuum dielectric constant, ε is the dielectric constant of the perovskite, *e* is the elementary charge, and *L* is the thickness film of the perovskite. *V*_{TFL} was obtained through

fitting the dark J–V curves. The perovskite film based on SnO₂ with GRT presented a much lower defect density of 3.17×10^{15} cm⁻³, as compared to 5.96×10^{15} cm⁻³ of the control

perovskite film, which was put down to the improved crystallinity and effective passivation of the quaternary ammonium cations and Cl⁻ anions in the GRT molecules for the anionic defects (e.g., Pb-I antisites and FA vacancy) and cationic defects (e.g., undercoordinated Pb or halide vacancies). Fig. 3g and h illustrate the PL mapping images of the perovskite films deposited on the non-conductive glass and GRT-coated glass substrates. Significantly enhanced photoluminescence (PL) intensities were found in the GRT-coated glass-based sample compared with the pure glass-based sample. This again confirmed that GRT can effectively passivate the defects at the surface of the perovskite films, which was consistent with the above SCLC result. In one word, high-quality perovskite films were fabricated after GRT modification for the SnO2 NPs. This indicates that the incorporation of GRT into the SnO2 NPs solution can improve the quality of not only the SnO₂ ETL films, but also perovskite films.

To uncover the effect of GRT modification on the interfacial electric contact, some effective characterization techniques were performed to gain deep insights into the interfacial carrier dynamics and recombination. Fig. 4a and b illustrate the steady state photoluminescence (SSPL) and time-resolved photoluminescence (TRPL) spectra of the perovskite films deposited on the non-conductive glass, SnO₂, and GRT-modified SnO₂ substrates. As shown in Fig. 4a, much better PL quenching was observed in the perovskite film based on GRT-modified SnO₂, as compared to the one based on SnO₂, which could be owing to the improved electronic property of the SnO₂ ETL and improved interfacial contact due to the chemical bridging between the SnO₂ ETL and perovskite layer by GRT molecules. The TRPL spectra in Fig. 4b were fitted by the following double exponential decay equation:¹³

$$I(t) = I_0 + A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_2 \exp\left(-\frac{t}{\tau_2}\right)$$
(2)

where τ_1 and τ_2 represent the fast attenuation component and slow attenuation component, respectively. It is generally recognized that τ_1 is related to the nonradiative recombination by defects/traps, and τ_2 is related to the radiative recombination from bulk perovskite.^{13,39,40} The average carrier lifetime (τ_{ave}) was calculated according to the following quation:^{13,39}

$$\tau_{\text{ave}} = (A_1 \tau_1^2 + A_2 \tau_2^2) / (A_1 \tau_1 + A_2 \tau_2)$$
(3)

The fitted lifetimes and the corresponding parameters are given in Table S1.[†] The perovskite film based on SnO₂ with GRT modification ($\tau_1 = 402.7$ ns, $\tau_2 = 1129.5$ ns, $\tau_{ave} = 1002.2$ ns) presented a much lower carrier lifetime than the one based on SnO₂ ($\tau_1 = 498.06$ ns, $\tau_2 = 2002.8$ ns, $\tau_{ave} = 1809.7$ ns), which indicates that the interfacial charge extraction was improved after GRT modification. Furthermore, the electron-transport yield (Φ_{tr}) of ETLs can be estimated by using the following formula:¹⁸

$$\Phi_{\rm tr} = 1 - \tau_{\rm p} / \tau_{\rm glass} \tag{4}$$

where $\tau_{\rm p}$ is the average lifetime of the perovskite deposited on different substrates, and τ_{glass} is the average lifetime of the perovskite film deposited on a glass substrate. The electron transport yield was prominently increased from 24.6% of SnO₂ ETL to 58.2% of GRT-modified SnO₂ ETL, which is consistent with the previous electron mobility measurement result. This indicates that GRT modification can effectively improve the quality and electronic properties of SnO₂ ETL. It was seen clearly that the TRPL results are in good accordance with the SSPL results. PL mapping images (500 μ m \times 500 μ m) of the perovskite films prepared on the SnO2 and GRT-modified SnO2 substrates are shown in Fig. 4c and d. Obviously, PL intensities were significantly decreased in a large area range for the perovskite film with GRT-modified SnO2 compared with the control film, which reflected the uniformity of our perovskite films and confirmed the reliability of the above SSPL and TRPL results. It is well-known that the interfacial charge extraction and transfer are greatly dependent on the built-in potential $(V_{\rm bi})$ of the devices.9,11 In order to further study the interfacial carrier dynamics, we measured the Mott-Schottky curves of the devices based on SnO₂ and GRT-modified SnO₂ ETLs, as shown in Fig. S8.† Vbi can be obtained by linearly fitting the Mott-Schottky curves. The V_{bi} was increased from 561 mV of the control device to 604 mV of the target device with GRT. Enhanced V_{bi} helped to promote the charge transfer and transport, which led to the reduced interfacial charge accumulation and interfacial nonradiative recombination. Then, the transient photocurrent (TPC) and transient photovoltage (TPV) were performed to investigate the charge transfer and recombination of the devices with SnO₂ and GRT-modified SnO₂, respectively. As exhibited in Fig. 4e, the device with SnO_2 (6.83) µs) gave a much higher carrier lifetime than the device with GRT-modified SnO_2 (2.33 µs), indicating the improved charge extraction and transfer, which is in excellent agreement with TRPL and built-in potential results. These results suggest that the GRT modification markedly improved the electron-selective contact of the SnO₂/perovskite interface. As presented in Fig. 4f, the carrier lifetime was enhanced from 3.32 μ s of the control device to 5.27 µs of the device with GRT addition, which was indicative of the remarkably suppressed nonradiative recombination. The reduced nonradiative recombination should mainly originate from the improved interfacial selective contact, and the improved quality of the SnO2 ETL and perovskite layer. The ideality factor (m) was extensively proposed to reliably evaluate the recombination in PSCs.8,41 Since it is so, we calculated the m values of the devices based on SnO₂ ETL and GRT-modified SnO₂ ETL through measuring the light intensitydependent $V_{\rm OC}$, as shown in Fig. 4g. As *m* approaches closer to 1, there is less trap-assisted nonradiative recombination in the devices.^{8,41} Consequently, the much lower *m* of 1.02 of the GRTmodified device than 1.38 of the control device with pristine SnO₂ indicated that GRT modification can effectively suppress nonradiative recombination, which was consistent with the TPV results. The electrochemical impedance spectroscopy (EIS) technique has been widely used to characterize the interfacial charge transfer and recombination.13,39 Fig. 4h exhibits the Nyquist plots of the devices based on SnO2 and GRT-modified

SnO₂, which was measured at a bias of 0.8 V in the frequency range of 1 MHz to 0.1 Hz under one sun illumination. The equivalent circuit diagram in Fig. S9[†] was utilized to fit the EIS spectra, and the corresponding fitting results are presented in Table S2.† Two semicircles were clearly observed. It was reported that the semicircle in the high-frequency region is closely related to the charge transfer and transport resistance (R_{ct}) , and the semicircle in the low-frequency region is put down to the recombination resistance $(R_{\rm rec})$.^{42,43} After GRT modification, the series resistance (R_s) and R_{ct} were slightly reduced, and $R_{\rm rec}$ increased significantly from 1356 Ω to 2526 Ω , as shown in Table S2.[†] Reduced R_s is ascribed to the improved quality of SnO_2 and perovskite films after GRT modification. Reduced R_{ct} is related to the improved electric property of SnO2 ETL and improved interfacial extraction, as confirmed by TRPL and TPC results. The increased $R_{\rm rec}$ is attributed to the suppressed interfacial nonradiative recombination due to the effective passivation of interfacial defects and improved interfacial contact. Obviously, compared to PSCs based on SnO₂, the device with $SnO_2 + GRT$ shows a smaller R_{ct} and larger R_{rec} . The small $R_{\rm ct}$ is beneficial for electron extraction, and the large $R_{\rm rec}$ effectively resists charge recombination, which agrees with the observations discussed above. These indicate that the electron extraction is improved, and the interface recombination is reduced by the introduction of GRT in SnO₂.

Since the improved quality of SnO₂ and perovskite films together with improved interfacial contact, we fabricated the planar devices with a structure of ITO/SnO₂ or SnO₂ + GRT/ $Rb_{0.05}(FA_{0.95}MA_{0.05})_{0.95}PbI_{2.85}Br_{0.15}/spiro-OMeTAD/Au$ to evaluate the effect of GRT modification on the device performance. First, the effect of GRT concentrations on device performance

was compared, as shown in Fig. S10,† and the average and best photovoltaic parameters are exhibited in Table S3.[†] Evidently, the optimal device performance was obtained at the concentration of 0.5 mg mL⁻¹ GRT. The average J_{SC} , V_{OC} , FF, and PCE were increased from 21.98 \pm 0.19 mA cm⁻², 1.083 \pm 0.009 V, 0.803 \pm 0.004, and 19.23 \pm 0.32% of the control device to 22.67 \pm 0.20 mA cm $^{-2}$, 1.139 \pm 0.004 V, 0.817 \pm 0.003, and 21.19 \pm 0.22% of the device based on 0.5 mg mL^{-1} GRT, respectively. Much improved V_{OC} along with slightly enhanced J_{SC} and FF contributed to the improved PCE. The improved J_{SC} could be ascribed to the slightly enhanced light harvesting ability, as confirmed by the slightly increased UV absorption intensity, electron extraction efficiency, as confirmed by the TRPL and TPC results, and charge collection efficiency, as revealed by improved charge transport due to the improved quality of SnO₂ ETL and perovskite films. The improved carrier transport in both SnO₂ ETL and perovskite films should be mainly responsible for the enhanced FF, which was supported by the reduced $R_{\rm s}$. Finally, the improved $V_{\rm OC}$ was mainly put down to the reduced bulk and interfacial nonradiative recombination, which resulted from the improved charge transport in the SnO₂ and perovskite films, and effective passivation of GRT for interfacial defects, as confirmed by reduced defect density (SCLC result) and increased carrier lifetime (PL mapping). The enlarged perovskite grain size and vertically orientated perovskite grains should be conducive to carrier transport. Excellent reproducibility was observed for the device with GRT modification (Fig. 5a). The hysteresis index (HI) was calculated by the formula

$$HI = (PCE_{RS} - PCE_{FS})/PCE_{RS}$$
(5)



Fig. 5 (a) Statistical distribution of PCE of the PSCs based on the SnO_2 and SnO_2 -modified by GRT of 0.5 mg mL⁻¹ calculated from individual 20 cells. (b) Statistical hysteresis index (HI) distribution calculated from individual 20 cells. (c) J-V curves and (d) corresponding IPCE spectra of the best-performing devices based on SnO_2 and GRT-modified SnO_2 . J-V curves were measured in the reverse scan (RS) and forward scan (FS) at a scan rate of 100 mV s⁻¹ under simulated AM 1.5 G one sun illumination of 100 mW cm⁻². The steady-state current density and PCE *versus* time for the best-performing devices employing (e) SnO_2 and (f) GRT-modified SnO_2 measured at the maximum power point.

where PCE_{RS} and PCE_{FS} represent the PCE in the reverse scan (RS) and the PCE in forward scan (FS), respectively. The *J–V* curves of the PSCs based on SnO_2 and $SnO_2 + GRT$ (0.5 mg mL⁻¹) are exhibited in Fig. S11.† As shown in Fig. 5b, the average HI was substantially reduced from 0.038 ± 0.005 to 0.014 ± 0.003 after GRT modification. Presently, the interfacial charge accumulation originating from the poor charge extraction and interfacial trap-assisted nonradiative recombination has been considered to be the main reason for *J–V* hysteresis.^{8,9,44} Therefore, the improved charge extraction and effective interfacial defect passivation could be responsible for the significantly suppressed hysteresis after GRT modification.

The J-V curves and incident photon-to-current conversion efficiency (IPCE) spectra of the champion control device and the target device with 0.5 mg mL⁻¹ GRT are exhibited in Fig. 5c and d, respectively. The corresponding photovoltaic parameters are shown in Table 1. The best-performing control device gave a J_{SC} of 22.45 and 22.64 mA cm⁻², a V_{OC} of 1.068 and 1.075 V, a FF of 0.798 and 0.812, and a PCE of 18.77% and 19.77%, in RS and FS, respectively. In contrast, the best-performing device with the optimal concentration of GRT delivered a J_{SC} of 22.91 and 22.92 mA cm⁻², a V_{OC} of 1.141 and 1.146 V, a FF of 0.812 and 0.823, and a PCE of 21.26% and 21.63%, in RS and FS, respectively. The integrated current density was estimated to be 22.24 mA cm^{-2} for the SnO₂-based devices and 22.88 mA cm^{-2} for the GRT-modified device, which were in excellent agreement with the J_{SC} from the J-V curves. Fig. 5e and f shows the stable output current density and PCE of the devices based on SnO2 and GRTmodified SnO₂, respectively. The current density and PCE of the device with SnO₂ were degraded from 20.46 mA cm⁻² and 19.64% to 18.49 mA cm^{-2} and 17.75% after 500 seconds, respectively (Fig. 5e). In comparison, a current density of 21.36 mA cm⁻² and a PCE of 21.3% of the device with GRT modification were still retained after 500 seconds (Fig. 5f). This indicates that GRT modification can improve the photostability of the device.

In order to reveal the effect of the GRT modification on the device stability, the moisture, thermal and light stabilities of the unencapsulated devices without and with GRT modification were measured and compared systematically. As shown in Fig. 6a and S12,† the device with GRT retained 96.4% of its initial PCE after exposure to the humidity of 5–10 RH% at room temperature in the dark for 1440 h, while 87.5% was retained for the control device under the same condition. This indicates that slightly improved moisture stability was achieved after GRT modification. Fig. 6b and S13† show the thermal stability of the

Table 1 Photovoltaic parameters of the best-performing devices without and with GRT modification measured in reverse and forward scan under AM 1.5 G 1 sun illumination of 100 mW cm⁻²

Devices	Sweep	$J_{ m SC} ({ m mA}~{ m cm}^{-2})$	$V_{\rm OC}$ (V)	FF	PCE (%)
SnO ₂	FS	22.64	1.075	0.812	19.77
	RS	22.45	1.068	0.798	18.77
$SnO_2 + GRT$	FS	22.92	1.146	0.823	21.63
	RS	22.91	1.141	0.812	21.26



Fig. 6 (a) PCE evolution of the unencapsulated devices based on SnO₂ without and with GRT modification exposed to the humidity of 5–10 RH% at room temperature in the dark. (b) PCE evolution of the unencapsulated devices based on SnO₂ without and with GRT modification aged at 60 °C in the dark, where the unencapsulated devices were located in the glovebox filled with nitrogen. (c) PCE evolution of the devices based on SnO₂ without and with GRT modification aged under one sun illumination at room temperature, where the devices were located in the glovebox filled with nitrogen.

unencapsulated devices based on SnO2 without and with GRT modification aged at 60 °C in the dark, where the unencapsulated devices were located in the glovebox filled with nitrogen. After aging for 720 h, up to 99.5% of its original PCE was maintained for the device with GRT, whereas only 46.5% was retained for the control device. Fig. 6c and S14[†] exhibit the photostability of the devices based on SnO2 without and with GRT modification aged under one sun illumination at room temperature, where the devices were located in the glovebox filled with nitrogen. The PCE of the control device was degraded by 80.7% after aging for 672 h, while the PCE of the device with GRT was degraded only by 41.5%. Trap-assisted nonradiative recombination has been widely considered to be one of the important reasons of device degradation.8,9,13,45-47 In our case, the enlarged grain sizes, reduced interfacial defects, and improved electron mobility of SnO2 led to significantly reduced bulk and interfacial nonradiative recombination losses, which should be mainly responsible for the improved stability.

Conclusions

In summary, we have demonstrated a novel simple and effective multifunctional modification strategy, where GRT molecules

with multiple functional groups are employed to modify the SnO₂ nanoparticles (NPs). The GRT modification has achieved the following three functions: first, the electrical property and the quality of the SnO₂ films are improved due to suppressed nanoparticle agglomeration via the strong chemical interaction between GRT and SnO₂. Second, the enlarged grain size and vertical growth of the perovskite crystals are realized, which are owing to the improved wettability and reduced roughness of the SnO₂ substrate. Finally, interfacial defects are reduced through the effective passivation of the quaternary ammonium cation and chloride in GRT for anionic and cationic defects at the surface of the perovskite films. As a result, the PCE is increased from 19.77% to 21.63% after GRT modification, along with significantly suppressed hysteresis. The improved stability is demonstrated for the device with GRT modification, as compared to the control device. The unencapsulated device with GRT retains 99.5% of its initial PCE after aging at 60 °C for 720 h, and 58.5% after aging for 672 h under one sun illumination. The improved efficiency, suppressed hysteresis, and enhanced stability are ascribed to the more suppressed bulk and interfacial nonradiative recombination. This result strongly suggests that it is feasible and effective to simultaneously enhance the efficiency and stability of PSCs by the rational engineering of multifunctional modification molecules. This work provides a guidance for the design of multifunctional modification molecules containing multiple functional groups toward the realization of highly efficient and stable PSCs.

Experimental section

Materials

The SnO₂ colloid precursor was obtained from Alfa Aesar (tin(v) oxide, 15% in H₂O colloidal dispersion). Girard's reagent T (98%) and rubidium iodide (RbI, 99.9%) were purchased from Aladdin. Lead(π) iodide (PbI₂, 99.99%) and methylamine hydrochloride (MACl, 99.5%) were purchased from Xi'an Polymer Light Technology Corp. Lead(π) bromide (PbBr₂, 99.999%), and spiro-OMeTAD (99.86%) were purchased from Advanced Election Technology Co., Ltd. Methylammonium bromide (MABr) and formamidine hydroiodide (FAI) were purchased from GreatCell Solar. *N*,*N*-Dimethylformamide (DMF, 99.8%), dimethyl sulfoxide (DMSO, 99.9%), and chlorobenzene (CB, 99.8%) were bought from Sigma Aldrich. All chemical reagents were used as received without further purification.

Device fabrication

ITO-coated glass substrates were etched by laser. The etched ITO glass was ultrasonically cleaned for 20 min using detergent, deionized water, and ethanol, sequentially. After the ITO substrates were treated by UV ozone (UVO) for 20 min, the colloidal solution of SnO_2 was spin-coated on the ITO substrates at 4000 rpm for 30 s, and then the as-prepared SnO_2 films were annealed at 150 °C for 30 min. The SnO_2 colloidal solutions without GRT were prepared by diluting the SnO_2 colloidal solution of 15 wt% to 2.14 wt% with deionized water. In the case of the GRT-modified solution, different concentrations of GRT

 $(0, 0.25, 0.5, 0.75, and 1 \text{ mg mL}^{-1})$ were added to the above diluted SnO₂ colloidal solution. After the films were cooled down to room temperature, the SnO2 films were exposed to UVO for 10 min. The 1.5 M perovskite precursor solution was prepared by dissolving FAI of 232.8 mg, MABr of 8.0 mg, RbI of 15.9 mg, MACl of 36 mg, PbI2 of 656.9 mg, and PbBr2 of 27.5 mg in the mixed solvents of DMF and DMSO ($V_{\text{DMF}}: V_{\text{DMSO}} = 8:1$). The perovskite films were prepared through spin-coating the above as-prepared perovskite precursor solution on the SnO₂ films at 4000 rpm for 30 s, where 80 µL CB antisolvent was dripped on the perovskite films at 14 s before ending the program. The wet perovskite films were annealed at 155 °C for 23 min. The spiro-OMeTAD solution was prepared by dissolving 72.3 mg spiro-OMeTAD in 1 mL chlorobenzene, which was followed by adding 28.8 µL of 4-tert-butyl pyridine (tBP) and 17.5 µL of lithium bis(trifluoromethanesulfonyl)imide (Li-TFSI) stock solution (520 mg Li-TSFI in 1 mL acetonitrile) into the above solution. Finally, a 80 nm-thick gold counter electrode was thermally evaporated on the top of the spiro-OMeTAD film under a vacuum of 3×10^{-4} Pa by using a shadow mask.

Characterization

J-V curves were measured using a solar simulator equipped with 150 W Xenon lamp (150 W, SolarIV-150A) and a Keithley 2400 source meter. The light intensity was calibrated to AM 1.5 G one sun (100 mW cm⁻²) with a NIM calibrated standard Si solar cell (QE-B1). The effective active area of the device was defined to be 0.07 cm^2 by using a black metal mask. The *J*-*V* curves were measured from -0.1 V to 1.2 V (forward scan) or from 1.2 V to -0.1 V (reverse scan) with a scan rate of 100 mV s⁻¹. The incident photon-to-current conversion efficiency (IPCE) measurement was conducted on an IPCE measurement system. Impedance spectroscopy was measured by an Electrochemical Workstation (China), and the data were analyzed by the Z-View program. UV-Vis absorption spectra were measured on a UV-Vis spectrometer (Shimadzu UV-1800, Japan). The contact angle goniometer (YIKE-360A model; Chengde Precision Test Instrument Factory, China) was employed to measure the contact angles. The SEM images were acquired using field-emission scanning electron microscopy (JSM-7800F, Japan). The FTIR spectra were recorded with a Nicolet iS50 Infrared Fourier transform microscope by Thermo Fisher Scientific (America). Time-resolved photoluminescence (TRPL) and steady-state photoluminescence (SSPL) spectra were measured using Edinburgh FLS1000 (UK), where the excitation wavelength of TRPL was provided by a 450 nm laser. Atomic force microscopy (AFM) measurements were carried out on Asylum Research MFP-3D-BIO (US) in tapping mode. The zeta potential and DLS measurement were tested on a Brookhaven NanoBrook Omni (US). XPS spectra were obtained using a Thermo-Fisher ESCA-LAB 250Xi system with a monochromatized Al Ka (for XPS mode) under the pressure of 5.0 \times 10⁻⁷ Pa. X-ray diffraction (XRD) spectra were recorded by a PANalytical Empyrean (Netherlands), and the incident angle of GIXRD was 0.5°. TPV and TPC measurements were performed as follows: the devices were illuminated by laser pulses (532 nm, 100 mJ, 6 ns width from an

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Nd:YAG laser), and then the decay of signals was recorded by a 1 GHz Agilent digital oscilloscope (DSO-X3102A) with input impedance of 1 M Ω /50 Ω . PL mapping spectra were recorded using a micro-confocal Raman spectrometer (LabRAM HR Evolution, France) with an excitation wavelength of 532 nm. Two-dimensional GIWAXS images were conducted at BL1W1A at Beijing Synchrotron Radiation Facility (BSRF) ($\lambda = 1.54$ Å). The incidence angle is 0.16° and the exposure time is 100 s.

Author contributions

H. B. and J. C. conceived the idea and designed the experiments. H. B. fabricated the devices and conducted the characterization. All authors participated in data analysis and discussion. J. C. supervised the project. H. B. and J. C. wrote the paper. All authors reviewed the paper.

Conflicts of interest

There are no conflicts to declare.

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