Materials & Design 228 (2023) 111850

Contents lists available at ScienceDirect

Materials & Design

journal homepage: www.elsevier.com/locate/matdes

High-efficiency tin perovskite solar cells by the dual functions of reduced voltage loss and crystal regulation



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HIGHLIGHTS

- PEACI is used for forming an ultrathin low dimensional perovskite layer at the interface of FASnI₃ perovskite and PCBM layer.
- The effective suppression of Sn²⁺ oxidation, the improved band level alignment and the decrease of the surface defect density is achieved by the PEACl treatment.
- Significantly enhanced conversion efficiency of tin-based PSCs can be obtained from 9.40% to 11.63% by the PEACl treatment.

ARTICLE INFO

Article history: Received 8 December 2022 Revised 12 February 2023 Accepted 18 March 2023 Available online 22 March 2023

Keywords: Tin perovskite solar cells Defect passivation 2D Materials Reduced voltage loss Crystal regulation

GRAPHICAL ABSTRACT

PEACI is employed to treat the pristine FASnl₃ film, leading to forming an ultrathin low-dimensional perovskite layer at the interface of perovskite and adjacent transporting layer. Finally, the treatment results in the enhanced stability and conversion efficiency from 9.40% to 11.63% by improving the crystallinity and interface, suppressing Sn²⁺ oxidation, decreasing defect density and well-matched energy level.



ABSTRACT

Environment friendly tin perovskite solar cells (TPSCs) have become a promising candidate due to their low toxicity and similar electronic configuration to lead counterparts. However, the easily generated defects due to the Sn^{2+} oxidation and poor morphology originated from rapid crystallization are both barriers for tin-based devices in the enhancement of photovoltaic performance. Here, phenethylammonium chloride (PEACl) is introduced for post-treating FASnl₃ films, which plays dual roles in adjusting film topography and passivating defects in bulk and interface of films. First, the film morphology can be improved by eliminating SnF_2 impurities. In addition, a small amount of two-dimension perovskite can be formed in the films, inducing preferred orientation in secondary crystallization, well-matched energy level, and effective defect passivation. Finally, the FASnl₃-based devices with PEACl treatment obtained a champion conversion efficiency of 11.63% with an average value of 10.76%, along with the obvious enhanced open circuit voltage and fill factor. In contrast, the pristine FASnl₃ devices range from 6.92% to 9.40% with an average value of 7.96%. This work not only deepens our understanding of the

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suppression of defects in tin-based perovskites but also paves a facile way to ameliorate film morphology and interfaces to fabricate promising tin perovskites and devices.

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1. Introduction

Organic-inorganic perovskite solar cells (PSCs) have gotten great attention, and the conversion efficiency of lead halides PSCs has proliferated to 25.7% [1] recently. However, the toxicity of lead to humans, ecology, and the environment may be a pending issue in the commercialization of lead-based devices^[2]. Consequently, environmentally friendly lead-free PSCs have triggered more interest, such as tin (Sn)[3–7], germanium[8], bismuth[9–11], antimony [12], etc. Among them, tin-halide perovskites have great potential as light absorber layers in photovoltaic performance due to their suitable band gap close to the Shockley-Queisser theoretical limit, high absorption coefficient, small exciton binding energy, and high carrier mobility [13]. Live up to expectations, tin-based perovskite solar cells (TPSCs) hold the highest conversion efficiency among all the lead-free photovoltaic devices so far, which has been pushed over 14%[14-16]. However, there is still a considerable gap compared to its theoretical efficiency or lead-based PSCs. This mainly may be ascribed to the poor quality of tin-based perovskite films, and the non-negligible open-circuit voltage loss (V_{loss}) due to the defects in the bulk and interface of films^[2].

In order to improve the crystalline quality of tin-based films, targeted methods have been applied [17-29], such as additive engineering[30–35] for controlling the nucleation and growth of grains. For example, piperazine dihydriodide is introduced to tune the crystallization kinetics of FASnI[36]₃ Films with prenucleation clusters, finally resulting in a high-quality perovskite film with low defect density[37]. Moreover, the material-dimension regulation also is explored to form low-dimensional tin-perovskites with oriented crystal growth by adding phenylethylammonium halides [38–41], 5-ammoniumvaleric acid[42], 2-hydroxyethylammonium [43], fluoro-phenethylammonium iodide[44], and ethylammonium iodide^[45], etc. The incorporated 2D components play a positive role in the orientation of films, suppression of Sn²⁺ oxidation, and defect passivation, resulting in the improvement of the photovoltaic property of tin perovskite films. In addition, interface engineering is an effective approach used to reduce V_{loss} by the improved energy level [46-48] and the defects passivation both in the bulk and at the interface of films[49].

Herein, we realized the morphology control and defect passivation of FASnI₃-based films by employing the phenylethylammonium chloride (PEACl). After the post-treatment of PEACl, the morphology of films can be improved by eliminating the impurities of SnF₂ on the surface of pristine FASnI₃ films. In addition, a small amount of two-dimension perovskite can be formed in the films, inducing preferred orientation in secondary crystallization, wellmatched energy level, and effective defect passivation. Finally, the significant enhancement in the power conversion efficiency (PCE) from 9.40% to 11.63%, with the obvious lower V_{loss}, can be achieved via introducing PEACl into the FASnI₃ TPSCs. Besides, the devices treated with PEACl also exhibit enhancement in stability.

2. Experimental section

Tin iodide (SnI₂, 99.99%), chlorobenzene (CB, 99.8%), tin fluoride (SnF₂, 99%), isopropanol (IPA, 99.7%), N, N-dimethylformamide (DMF, 99.8%), and dimethyl sulfoxide (DMSO, 99.8%) were obtained from Sigma-Aldrich. 1,1,4,4-Tetrahydro-di[1,4]methano

naphthaleno[1,2:2,3,56,60:2,3][5,6]fullerene- C_{60} (indene- C_{60} bisadduct, ICBA) were obtained from 1-Materials. Poly (3,4ethylene dioxythiophene)-poly (styrene sulfonate) (PEDOT: PSS) solution is purchased from Heraeus. Formamidinium Iodide (FAI), bathocuproine (BCP), and phenethylammonium chloride (PEACI) were purchased from GreatCell Solar (Australia). ITO glass is obtained from PV TECH with a sheet resistance of about 12 Ohms/sq. UV curing sealant was purchased from Blufixx for the edge sealing for tin-devices.

0.8 mmol/mL FASnI₃ precursor solutions were prepared by dissolving 0.8 mmol SnI₂, 0.8 mmol FAI and 0.08 mmol SnF₂ in 1 mL mixed solution with the volume ratio of DMF and DMSO is 4:1. The above solutions were totally dissolved into a transparent solution under stirring at 25 $^{\circ}$ C.

The ITO glass substrates were cleaned using detergent, deionized water, ethanol, acetone, and isopropanol in an ultrasonic bath for 20 min, sequentially. Then, the ITO glass substrates were dried and cleaned with UV-Ozone for 25 mins. After that, the PEDOT: PSS layers were deposited on the ITO glass substrates, by spin-coating at 5000 rpm for 40 s at 25 °C in the air, followed by annealing at 150 °C for 15 min. The Sn-perovskite films were performed in an N₂ glove box. The precursor solutions were filtered with a 0.22 μ m PTFE filter and dropped onto PEDOT: PSS/ITO substrates, subsequently spin-coating at the speed of 6000 rpm for 60 s. Then, 120 μ L CB is dropped down during the spinning process at about 30 s, and all the films were post-annealed at 80 °C for 10 mins. The room temperature is about 25 °C.

PEACl is dissolved in isopropanol with a concentration of 4 mg/mL. Then, the PEACl solution of 50 μ L is dropped onto the films at the speed of 6000 rpm, and the obtained films need to be annealed at 80 °C for 5 mins to form the low-dimensional perovskites.

To make an electron-extraction layer, $40 \ \mu L$ of ICBA ($20 \ mg/mL$ in CB) solution was spin-coated on the top of perovskite film at the speed of 1200 rpm for the 30 s. Finally, 5 nm BCP and 80 nm Al as top electrodes were evaporated on top of the film through a shadow mask by thermal evaporation to finish the device fabrication. The effective area of the devices is determined by the shadow mask of 0.4 cm × 0.4 cm.

X-ray diffraction (XRD) spectra were collected using the Rigaku MiniFlex600 X-ray diffractometer (Cu K α , 1.5406 Å). Top-view morphology of the perovskite films were measured by a high-resolution field emission scanning electron microscope (SEM, TES-CAM MIRA3). The absorption spectra were taken using a Shimadzu ultraviolet–visible spectrophotometer (UV-3600). Room-temperature photolunminescence (PL) spectra were measured by Spectrofluorometer (FS5, Edinburgh instruments) with a 405 nm pulsed laser.

X-ray photoelectron spectroscopy (XPS) measurements were carried out on an Omicron ESCA Probe XPS spectrometer (Thermo Scientific ESCALAB 250Xi) using 150 eV pass energy and 1 eV step size for survey scan and 20 eV pass energy and 0.01 eV step size for the fine scan. The XPS spectra were calibrated by the binding energy of 284.8 eV for C 1 s. To measure work function, ultraviolet photoelectron spectroscopy (UPS) spectra were recorded with an Imaging Photoelectron Spectrometer (Axis Ultra, Kratos Analytical Ltd), with a non-monochromated He I α photon source (h ν = 21.2 2 eV). Au is as a reference.

The current density-voltage (J-V) curves were measured by a Keithley 2400 source meter under AM1.5 spectrum (100 mW/

cm²) using the xenon arc lamp of a Sirius-SS300A solar simulator. Light intensity was calibrated using a monocrystalline Si-cell. The devices were measured in a reverse scan from 1.0 V to -0.2 V with 0.01 mV intervals, and a forward scan from -0.2 V to 1.0 V with identical intervals, with no any preconditioning, under the 25 °C and the average humidity of 80%. In addition, the J-V measurement is conducted in air, with the mask area of 0.08 cm². Due to the easy oxidization of tin perovskites, we use a simple encapsulation with the UV curing sealant to prevent humidity and oxygen from degrading of device performance.

The space charge limited current (SCLC) method was used to evaluate the trap-state density in the perovskite films. The dark I-V curves of the hole-only devices using the structure consisted of ITO/PEDOT: PSS/tin-perovskites/Poly (triaryl amine) (PTAA)/Au.

3. Results and discussion

To observe the effect of phenethylammonium chloride (PEACl) post-treatment onto the FASnI₃ perovskite films, X-ray diffraction (XRD) is applied to assess the crystallinity and structure of these films. It is easy to see that the obvious two-dimension (2D) perovskite peaks emerge, shown in Fig. 1a, compared to the pristine FASnI₃ one. In addition, the XRD intensity at (100) peak exhibits a slight enhancement, meaning the improvement in the crystallinity and orientation of the films with optimal PEACI. As shown in Fig. 1b, the UV-Vis absorption of the corresponding films displays a tiny shift on the edge with the incorporation of PEACl, resulting in potential light-absorption shrink, indicating the negative influence resulting from an overdose PEACI. The scanning electron microscope (SEM) is used for investigating the morphology and difference between the films with and without the PEACl. From the high magnification SEM images in Fig. 1c and 1e, the smoother and more uniform surface topography can be obtained after PEACl post-treatment. Especially, the excessive SnF₂ impurities apparently disappeared on the film surface, clearly shown in low magnification SEM images (Fig. 1d and 1f). The improved morphology should be beneficial to enhance the performance of the photovoltaic device.

As shown in Fig. 2, X-ray photoelectron spectroscopy (XPS) is measured to clarify the Sn²⁺ oxidation and elemental composition analysis in films without and with PEACl. In the Sn 3d XPS spectra of the pristine FASnI₃ without PEACl in Fig. 2a, there are two peaks at 486.3 eV and 487.1 eV deconvoluted from the Sn $3d_{5/2}$ peak, which is identified to Sn²⁺ and Sn⁴⁺, respectively. Similar peaks can be observed from the PEACl-treated films in Fig. 2b.

As summed in Table 1, there is a manifest decline in the fraction of Sn⁴⁺/Sn²⁺ from 12.7% to 6.5% in PEACI-treated films, compared with pristine FASnI₃ one. This is the quantitative evidence of inhibiting Sn²⁺ oxidation by applying PEACl. We can also observe an apparent difference between the pristine and optimal PEACIcontained films in the F 1 s spectra, shown in Fig. 2c. The PEACIcontained films show the lower intensity of the F 1 s peak, which likely originates from the reduction of SnF₂ impurity, in agreement with the surface morphology observed in SEM images. The Cl 2p spectra in Fig. 2d give an explicit confirmation of the presence of Cl in the films after PEACl treatment. Meanwhile, the emerged peak at about 402 eV can be featured to the N in 2D perovskites, further confirming the formation of 2D perovskites. In Fig. 2f, I 3d spectra show an enhanced intensity in the PEACl-contained films, which might due to the inhibition of I⁻ migration after incorporating 2D perovskites by PEACl application.

To investigate the optoelectronic properties of the pristine FASnI₃ and PEACl-contained films, ultraviolet photoelectron spectroscopy (UPS) measurements were performed and shown in Fig. 3a and 3b. The work function (WF) of the pure FASnI₃ films can be determined to be about -4.78 eV, deduced from the onset of UPS spectra (Fig. 3a), while the obvious shift to -4.47 eV occurred in the PEACl-contained film. According to the tail of UPS spectra in Fig. 3b, the corresponding valence band maximum (VBM) values of the pristine FASnI₃ and PEACl-contained films can be deduced to -5.16 eV and -5.09 eV, respectively. Furthermore, the bandgaps of the two kinds of perovskite films are calculated as 1.35 eV and 1.39 eV, from the corresponding Tauc plots (Fig. 3c), which is consistent with the previous reports. And finally, an energy-level diagram of the inverted planar TPSCs containing both the pristine FASnI₃ and optimal films with PEACl is shown in Fig. 3d. Notably, the optimal films with 2D perovskites have a



Fig. 1. (a) The X-ray diffraction (XRD) patterns of tin-perovskite films with and without PEACI. (b) UV–Vis absorption of these films with normalization. (c-f) Top view SEM images of tin perovskite films without or with PEACI: (c, d) w/o, (e, f) with PEACI.



Fig. 2. The X-ray photoelectron spectroscopy (XPS) spectra of Sn 3d of FASnl₃ films (a) without and (b) with PEACl. The XPS spectra of (c) F 1 s, (d) Cl 2p, (e) N 1 s and (f) I 3d of the tin perovskite films without and with PEACl treatment, respectively.

Table 1	
The fitting results of XPS spectra for the $FASnI_3$ and optimal films.	
	-

PEACI treatment		Sn 3d5/2		Sn 3d _{3/2}		Sn ⁴⁺ /Sn ²⁺
		Sn ²⁺	Sn ⁴⁺	Sn ²⁺	Sn ⁴⁺	
without	position	486.30	487.05	494.70	495.40	12.7%
	area	116287.65	14748.33	77563.86	9837.14	
with	position	486.25	486.95	494.65	495.35	6.5%
	area	115685.72	7570.87	77162.38	5049.78	

higher valence level and slightly wider band gap than the pristine FASnI₃ films, which shows the improved carrier collection and transport at interfaces between perovskite layer with both Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT: PSS) and indene-C60 bisadduct (ICBA), resulting in potential enhancement of the photovoltaic performance. Therefore, the photovoltaic performance of the pristine FASnI₃ and PEACI-contained films was investigated in devices with a configuration of ITO/PEDOT: PSS/tin-perovskites/ICBA/bathocuproine (BCP)/AI, and the corresponding current density–voltage (J-V) curves are shown in Fig. 3e.

We can clearly observe that the optimal PEACl-contained devices result in better performance with the champion PCE of 11.63%, the open circuit voltage (V_{OC}) of 0.75 V, the short circuit current density (J_{SC}) of 21.53 mA/cm² and the fill factor (FF) of 0.72. In contrast, the pristine FASnI₃-based device shows a relatively low PCE of 9.40 % with a J_{SC} of 21.25 mA/cm², V_{OC} of 0.66 V, and FF of 0.67. A significant increase on V_{OC} from 0.66 V to 0.75 V can be observed in the J-V curves, indicating the effective passivation of interface defects and inhibition of nonradiative recombination by forming the 2D perovskites and passivated Cl⁻ anions after the introduction of PEACl. The small enhancement on J_{SC} from 21.25 to 21.53 mA/cm² should be attributed to the improved carrier collection and transporting by optimal surface morphology of films and well-matched energy levels after PEACl

incorporation. The improvement of FF possibly is due to the interface engineering by treating with PEACl, especially the elimination of SnF₂ impurities. In addition, as shown in Fig. 3f, the optimal PEACl-contained devices display an ignorable hysteresis from the forward and reverse scans, in contrast with the pristine FASnI₃ ones. The improvement might be due to the well-matched energy-level alignment of the device, resulting in the facilitation of carrier extraction at the interfaces after introducing PEACl.

To investigate the reproducibility of the FASnI₃-based devices and the PEACl treatment process, multiple batches of devices with a sample size of 30 were fabricated and shown in Table 2 and Fig. 4. The PCE varies from 9.78% to 11.63% with an average value of 10.76% for the PSCs based on PEACl-contained films. In contrast, the control one ranges from 6.92% to 9.40% with an average value of 7.96%. It is easy to know that the pristine FASnI₃-based devices show relatively poor repeatability, especially wide distribution over J_{SC} and FF, as shown in Fig. 4. While the PEACl-contained devices exhibit remarkable and impressive photovoltaic performance with narrowing distribution on all the parameters.

The steady-state photoluminescence (PL) and the time-resolved photoluminescence (TRPL) spectra are measured and shown in Fig. 5, to investigate the carrier dynamics of the pristine FASnI₃ and PEACl-contained films, which is about the density of defect states. First, the obvious blue shift (900 to 880 nm) of the PL emis-



Fig. 3. (a) Ultraviolet photoelectron spectroscopy (UPS) spectra of the pristine FASnl₃ and PEACl-contained films (The work function (WF) is calculated by the equation: WF = $hv-(E_0-E_F(Au))$, where the $E_F(Au)$ is the Fermi level of reference Au). (b) Corresponding valance band spectra of the films without and with PEACl. (c) Tauc plots were obtained from the absorption spectra of films. (d) Energy-level diagram of the planar inverted PSCs containing both the pristine FASnl₃ and optimal films with PEACl. (e) The J-V curves of champion devices for the pristine FASnl₃ and optimal films with PEACl from the forward scan. (f) J-V curves of the champion device based on the pristine film and optimal PEACl-contained film from forward and reverse scans, respectively.

Table 2

Summary of photovoltaic performance based on the pristine FASnI_3 and $\mathsf{PEACl}\text{-}contained$ devices.

PEACI content	J _{SC} (mA/cm ²)	V _{OC} (V)	FF	PCE (%)
w/o	18.43 ± 1.63^{a} (21.25) ^{b)}	0.65 ± 0.02 (0.66)	0.67 ± 0.02 (0.67)	7.96 ± 0.53 (9.40)
with	20.7 ± 0.7 ^{a)} (21.53) ^{b)}	0.73 ± 0.01 (0.75)	0.71 ± 0.01 (0.72)	10.76 ± 0.53 (11.63)

^{a)} The averaged values of 30 devices from different batches; ^{b)} the values corresponding to the champion devices are in the parenthesis.



Fig. 4. The distribution of J_{SC}, V_{OC}, FF, and PCE based on pristine FASnI₃ and PEACI-contained devices. The sample size is 30 in both cases.



Fig. 5. (a) The steady-state photoluminescence (PL) and (b) time-resolved photoluminescence (TRPL) spectra of the pristine FASnl₃ and PEACl-contained films on the glass substrates. (c) The current–voltage of hole-only devices for measurement of the traps state of the pure FASnl₃ and PEACl-contained films (The traps state (n_{trap}) can be calculated by the following relation: $n_{trap} = 2\varepsilon\varepsilon_0 V_{TEL}/eL2$, where ε is the relative dielectric constant, ε_0 is the vacuum permittivity, V_{TFL} is the onset voltage of TFL region, e is the elementary charge, and L is the thickness of the perovskite films.). (d) The linear relationship of V_{OC} to the logarithmic light intensity for the FASnl₃ and PEACl-contained devices.



Fig. 6. (a) stability tests for the perovskite devices without and with PEACI for 60 days. (b) UV-vis absorption spectra of pristine FASnI₃ films and PEACI-contained tinperovskites after exposure to air for a different time under 25 °C and a humidity of 60%.

sion peak with applying PEACl onto the FASnI₃ films demonstrates the formation of a 2D perovskite phase and the incorporation of Cl⁻ anions, which is consistent with the bandgap shrinking obtained from light absorption. Then, the PL intensity is significantly increased for the PEACl-contained films, and the carrier lifetime of the optimal perovskite film shows over a 2-fold longer time than the pristine FASnI₃, according to the TRPL results in Fig. 5b, indicating the reduction of defect density by applying the PEACl to the tinperovskite films. Furthermore, to measure the trap states for evaluating carrier mobility of the perovskite films, space-charge limited current (SCLC) measurement was performed on the hole-only devices with a structure of ITO/PEDOT: PSS/tin-perovskites/Poly (triaryl amine) (PTAA)/Au. As shown in Fig. 5c, the onset voltage of the TFL region (V_{TFL}) is 0.22 V for the optimal PEACl-contained film, in contrast with 0.30 V of the pristine FASnl₃ perovskite, indicating a significant elimination of the traps state by constructing the 2D perovskite interface by applying PEACl post-treatment.

The light intensity-dependent V_{oc} of TPSCs with and without PEACl are both conducted and summed in Fig. 5d, in which slope (kT/q) is closely related to the trap-assisted recombination in the devices[50]. The optimal PEACl-contained device exhibits a smaller slope of 1.19 kT/q than the 1.52 kT/q for the control one, which indicates reduced energy loss from trap-assisted recombination, compared with the pristine FASnI₃ one. This is a further confirmation that the trap density is significantly suppressed by integrating the passivation of 2D perovskite and Cl⁻ anions, finally resulting in the impressed enhancement of device performance.

Meanwhile, we tracked the device's performance with encapsulation, in order to eliminate the interference of water and oxygen. As clearly shown in Fig. 6a, the efficiency of the PEACI-containing PSC retains 90% of its initial value for over 60 days, while the control FASnI₃-based device shows a sharp drop to 80% after 20 days. The absorption spectra (Fig. 6c) of the optimal films do not exhibit a significant change within 60 mins, while the absorption of the control films is significantly reduced under the same humidity of 60% at 25 °C, shown in Fig. 6b. This indicates that improved stability of the films with the low-dimensional perovskite interfacial layer might account for the improved device stability, which is in accordance with the former report.

4. Conclusion

In conclusion, PEACl is applied to post-treat the pristine FASnI₃ perovskite films with the improvement of film morphology, defects and traps, and surface engineering. First of all, the film morphology is more flatter and uniform with the elimination of SnF₂ impurities after treating PEACl onto the FASnI₃ perovskite films. And the preferred orientation and reduction of Sn²⁺ oxidation of films also demonstrate an improvement in the quality of polycrystalline films. In addition, with the formation of 2D perovskites and the passivation of Cl⁻, the optimal PEACl-contained films have lower defects and trap density. All the improvement leads to the remarkably enhanced photovoltaic performance of PSCs with the effective conversion efficiency up to 11.63% from 9.40% of the pristine FASnI3 one. This work brings us a facile method of modulation engineering for obtaining high-quality tin-perovskite films by designing 2D/3D mixed films. Besides this work definitely deepens our understanding of the suppression effect of PEACI molecule on the oxidation of Sn²⁺ and defects in the tin-perovskites, and gain insight into the relationship between defects and photovoltaic performance in TPSCs.

Data availability

Data will be made available on request.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

The authors thank Mr. Huqiang Yi from the Southwest University of Science and Technology (SUSTech) for some characterizations in this research. This work is supported by the Guangdong Basic and Applied Basic Research Foundation (Joint Fund, No. 2019A1515111134), Startup funding from local government (827/000544), and High-level university construction fund (860-000002081205), the National Natural Science Foundation of China through grants (51973119), the Guangdong Basic and Applied Basic Research Foundation (Joint Fund, No. 2019A1515111134), and Open Project of Key Lab of Special Functional Materials of Ministry of Education, Henan University (KFKT-2022-10), the Guangdong Provincial Key Laboratory of Durability for Marine Civil Engineering (SZU) (Grant No. 2020B1212060074).

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