Kelvin probe force microscopy for perovskite solar cells

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ABSTRACT Kelvin probe force microscopy (KPFM) could identify the local work function of surface at nanoscale with high-resolution on the basis of simultaneous visualization of surface topography, which provides a unique route to *in-situ* study of the surface information like the composition and electronic states. Currently, as a non-destructive detection protocol, KPFM demonstrates the unique potential to probe the basic nature of perovskite materials that is extremely sensitive to water, oxygen and electron beam irradiation. This paper systematically introduces the fundamentals and working mode of KPFM, and elaborates the promising applications in perovskite solar cells for energy band structures and carrier transport dynamics, trap states, crystal phases, as well as ion migration explorations. The comprehensive understanding of such potential detection engineering may provide novel and effective approaches for unraveling the unique properties of perovskite solar cells.

Keywords: Kelvin probe force microscopy, perovskite solar cells, carrier transport dynamics, trap states, ion migration

INTRODUCTION

Kelvin probe force microscopy (KPFM) also known as surface potential microscopy which detects the local surface potential with high resolution of nanometer scale offers extensive applications in the research of photovoltaic devices, semiconductors and metals structure [1–4]. Initially, Kelvin probe method, was first proposed by Lord Kelvin in 1898 [5], restricted to detect the contact potential difference (CPD) merely between connected metals. Afterward, a simple method was put forward by Zisman in 1932 [6] to acquire a high resolution of CPD up to 1 mV by utilizing Kelvin probe which was limited to

measuring the average surface potential of metal samples. Until 1991, with the advent of scanning probe microscopy (SPM), Nonnenmacher *et al.* [7] developed a new function in KPFM, which can measure the local electrostatic potential. Over the past 20 years, KPFM has gradually received attention and its applications range from metal/semiconductor structures to perovskite solar cells [8–14].

Perovskite solar cells are the third generation of new concept solar cells with high conversion efficiency, which is a new compound thin film solar cell developed in recent years and becomes a global research hotspot [15–18]. Even though the energy conversion efficiency of perovskite solar cells has increased rapidly and reached above 23% so far [19], the lack of comprehensive understanding of perovskite materials and the stability restrict their further development [20–26]. Especially, the potential difference due to the different energy band structures directly influences the spatial transportation of carriers, but the deep insights into the behavior of localized photogenerated charges are limited [27–30]. Moreover, the anomalous current-voltage hysteresis under different bias directions [31–35], trap states-induced non-radiative recombination [34,36–39], phase segregation-induced degradation [40], and ion migration [41–45] also influence the development pace of perovskite solar cells towards commercial applications. Thus, it is of great significance to unveil the origin and nature of such phenomena and overcome the problems [46–49]. Several advanced characterization techniques demonstrate the competitive superiorities to trace, visualize and quantify the operational process [50]. Unfortunately, perovskite materials decompose facilely in water, oxygen, illumina-

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tion and electron beam irradiation, which further increases the difficulty of characterizations [51–53]. KPFM could identify the local work function of the surface at nanoscale with high-resolution on the basis of simultaneous visualization of sample topography, which provides a unique route for *in-situ* studies of the composition, electronic states, energy band-bending, charge trapping, and surface reconstruction, which are related to the surface photovoltage and CPD [54–56]. Notably, compared with other characterization techniques, KPFM does not require complicated sample preparation and is implemented in a non-contact mode, to immensely minimize the damage of the sample [57,58]. The unique advantage of KPFM for work function detection shows the promising potential to probe the basic nature of environment-sensitive materials and the operation mechanism of related devices [59–62].

In this review, we highlight the fundamental principle, working modes, instrumental parts and the development in KPFM and systematically summarize its application in perovskite solar cells. The relevant core-problems about the energy band structures and carrier transport dynamics, trap states, crystal phases as well as ion migration exploration have been elaborated in detail.

FUNDAMENTALS OF KPFM

On the basis of atomic force microscope (AFM), KPFM is developed with the combination of the macro-Kelvin probes [63]. The cantilever of the AFM is a force sensor with high sensitivity and its vibration depends on the tip-sample interaction, which can measure the CPD even if the capacitance between the probe and sample is extremely tiny, while KPFM considers the tip-sample system as a capacitor [64].

The research shows that the surface work function depends on the energy distinction between the vacuum level and Fermi energy level [58,65]. When there is an electrical contact between two substances, the process that electrons flow from one side with a small work function to the other side with a large work function produces the opposite charges on the substances, leading to the formation of CPD and inducing an electric field [66]. As a result, the electrostatic force is generated between the tip and sample due to the difference between their Fermi levels. In a KPFM system, an alternative voltage (V_{AC}) and a direct voltage (V_{DC}) are introduced to the tip, where the V_{AC} produces electrostatic oscillations and the V_{DC} eliminates the electrostatic oscillations caused by potential difference between the tip and the sample [67]. A lock-in amplifier which is not sensitive to

V_{DC} is utilized to track the vibration of the cantilever and obtain the CPD through the extraction of the electrostatic force. By controlling V_{DC} equal to CPD through the feedback loop, the output signal of lock-in amplifier that is proportional to the difference between CPD and V_{DC} is eliminated, namely the cantilever vibration amplitude is eliminated. In this way, we can find that the electric field and charges are eliminated through the external bias V_{DC} to the system as a bulking voltage. Therefore, once we obtain the work function of a tip (marked as Φ_{tip}), the work function of a sample (marked as Φ_{sample}) can be acquired by a simple formula: $\Phi_{sample} = \Phi_{tip} - e \times \text{CPD}$, where e is the electronic charge [68]. At the same time, we can obtain a defined formula of CPD between the conductive AFM tip and a sample surface by transforming the above formula to another form: $\text{CPD} = (\Phi_{tip} - \Phi_{sample})/e$.

Here, we use a visual diagram to understand CPD thoroughly. Fig. 1a–c show the energy level diagram of the tip and sample surface in three states [57]. First, as shown in Fig. 1a, at a certain distance of d , the sample and the tip present different Fermi level and have no electrical interaction. In Fig. 1b, the tip and the sample are close enough to keep electric contact. As previously described, the electrons will transfer from the sample to the tip resulting from their different work functions which will generate a CPD and finally their Fermi levels will keep constant in a line, reaching an equilibrium [69]. Fig. 1c shows the previous state as shown in Fig. 1a because when we add an external bias V_{DC} that is equal to the CPD between the tip and the sample, the surface charges are eliminated on the tip and the sample.

KPFM is an instrument based on the non-contact atomic force microscopy [66]. Hence, KPFM can detect the local surface potential by two working modes: amplitude modulation mode (AM) and frequency modulation mode (FM) [70]. The topography of the sample surface and CPD between the tip and the sample can be detected in both AM and FM mode, whereas their resolution is different due to different measuring mechanisms. AM-KPFM aims to eliminate the electric force which achieves a super high energy resolution while FM-KPFM with high spatial resolution [68,71] aims to eliminate the electric force gradient. At present, it is still indispensable to enhance the resolution of KPFM in response to its wide application.

As above, we make a comparison of the AM and FM mode in some respects. Primarily, they have similarity in external bias: an AC bias V_{AC} at frequency ω_{AC} plus a DC bias V_{DC} are applied between the tip and sample. In the AM-KPFM, meanwhile an electric force consisting of

Figure 1 (a–c) Three conditions of energy levels of the sample (S) and the tip (T): (a) The tip and sample surface have no contact. (b) The tip and sample have contact and their Fermi levels keep constant. (c) Applying an external bias (V_{DC}) with adverse direction between the tip and sample. E_V is the vacuum energy level. (d) The setup schematic diagram of both AM-KPFM and FM-KPFM. The bold line indicates the FM-mode and the dashed line indicates the AM-mode [70]. Copyright 2010, Elsevier B.V.

three compositions (F_{DC} , F_w , F_{2w}) is generated, where F_w and F_{2w} are single and double frequency AC electrostatic force, respectively. If we regulate V_{DC} to equal to the CPD, F_w would reduce to zero, inducing a null value to the amplitude of cantilever. Besides that, AM-KPFM can still be further divided into other two modes: a dual pass process and dual frequency mode. The former fits small transformation in potential while the latter fits large potential transformation. An electric force gradient consisting of three elements ($\partial F_{DC}/\partial z$, $\partial F_w/\partial z$, $\partial F_{2w}/\partial z$) is generated in the FM-KPFM. It is prevalent to utilize the resonance frequency (ω_0) shift of cantilever to detect electric force gradient. Regulating V_{DC} to eliminate the two side peaks of ω_0 cancels the electric force gradient [66,71].

Finally, we illustrate several significant schematic setup and components of KPFM [71]. Fig. 1d contains lock-in amplifier, frequency and amplitude regulation system. The vibration state of the probe detected by a beam deflection is transformed to a signal exported from the position sensitive photodiode (PSD), which later goes into frequency and amplitude regulation system to be detected. Therefore, lock-in amplifier is an essential composition which is sensitive to detect phase. According to the setting principle of lock-in amplifier, we could

consider it as a blender where two signals blend together. The export of the blender may be a DC voltage or others which hinge on the frequency of two signals. The lock-in amplifier with AM mode is applied to read high frequency signals from a band-pass filter after an output from PSD that is shown by dash line indicated in Fig. 1d. In the FM mode, the lock-in amplifier directly reads the signal from frequency regulation system and detects the frequency deviation caused by electrostatic force [64]. In addition, here the lock-in amplifier regulates the DC bias by inputting the signal to the KPFM controller. Eventually, the topography and CPD are received through the above measurement set-up apparatus [69,72].

APPLICATION OF KPFM

Energy band and carrier transport dynamics analysis

The charge generation and extraction within the perovskite are the key to the overall device performance. The energy band matching of different layers is of vital importance for the efficient charge transfer [73–77]. The ultraviolet photoemission spectroscopy (UPS) has been widely used to explore the position of energy levels [78]. But there are many requirements for testing samples, such as high conductivity and suitable size [79]. Different from UPS, KPFM could detect the work function of various materials under lighting and heating conditions [63]. Through the potential offset between the probe tip and the material surface, the CPD which is equal to the difference of work function of the AFM probe tip and the sample can be acquired in nanoscale. Hence, the Fermi level of the detected material could be acquired easily. Currently, KPFM has been widely used to acquire the energy band structures. Especially, the energy band structure of the SnO_2 -based electron transport layer is detected by KPFM [80]. The mapping of the work function demonstrates that the Fermi level of SnO_2 with ethylene diamine tetraacetic acid is closer to the conduction band of perovskite than that of the pure SnO_2 . KPFM is also applied to identify the energy band position of perovskite with Cu^+ doping [81]. The change of Fermi level proves that the addition of Cu^+ is a promising strategy to modulate the band structure for matching energy bands. For all-inorganic CsPbBr_3 perovskite quantum dots sensitized solar cells, the anomalous potential distribution in different layers of solar cells under different illumination is obtained by KPFM [82].

The accumulation of carriers induces an un-negligible effect on the potential, which has been investigated by

KPFM. In Fig. 2 of the cross-sectional potential distribution, there is a uniform electric field in the perovskite solar cells in the dark. However, when the devices are exposed to white light, the separation and transmission of photogenerated electrons and holes increases, while the CPD of the hole transport layer and the electron transport layer decreases. Meanwhile, the accumulation of holes at the hole transport layer and perovskite interface also indicates that the extraction efficiency of holes in the device is lower than that of

electrons in electron transport layer. Hence, the potential distribution in perovskite solar cells is significantly affected by carrier accumulation, which is corresponding to the work functions between different layers. In addition, the distribution of charge under different wavelength (ultraviolet, green and red) illumination is also investigated. Thus, both TiO_2 and perovskite can be excited by ultraviolet light. Because the conduction band of electron transport layer is occupied by the self-excited electrons, it is difficult for the perovskite's electron to jump in electron transport layer, while the excess electrons lead to the CPD reduction of electron transport layer. Under the green light, the distribution of CPD is similar to that under white light, while the perovskite cannot excite charge carriers under monochromatic light as much as that under white light, which leads to a poor surface potential difference. As the red light is not enough to excite perovskite, the surface potential does not change significantly when there is barely no carrier generation or accumulation in the perovskite solar cells.

KPFM is also utilized to identify the charge separation location in perovskite solar cells with typical mesoporous and planar structures by tracing the potential fluctuation [83]. The major potential drop exists at the perovskite/mesoporous TiO_2 interface for the mesoporous structured perovskite solar cell. While potential fluctuation for planar perovskite solar cells is at both sides of the perovskite layer. The position of the potential drop can be changed from the perovskite/ TiO_2 interface to perovskite/hole transport layer interface by incorporating excess PbI_2 . It indicates that the distribution of the electrical potential in the planar perovskite solar cells is sensitive to the composition of the perovskite, which can be easily tuned by changing the component of the perovskite. KPFM provides the charge separation and transmission images by detecting the surface work function. Both the energy band structure and carrier transport dynamics have been investigated by KPFM, which promotes the development of perovskite solar cells [84,85].

Trap states investigation

Energy levels of impurity atoms are inevitably introduced into the band gap during fabricating perovskite process. If trap states are located on the surface of the material, some additional energy levels become surface states. Meanwhile, crystal defects and impurities in the grain boundaries result in the formation of trap states level which may act as non-radiative recombination sites in the band gap. To investigate trap states in perovskite materials, KPFM is a powerful protocol for not only

Figure 2 (a–e) Surface potential images across the cross section of the solar cell under dark condition, solar illumination, shorter (UV), medium (green), and longer (red) wavelength of light, respectively. (f–j) Potential depth profiles across the layers of the solar cell under dark condition, solar illumination, UV, green, and red light illuminations, respectively. (k) (i) Vacuum level alignment along n-type/perovskite/p-type material in solar cell before contact. (ii) Fermi level alignment after contact in the dark (equilibrium condition). (iii) Separated quasi-Fermi levels for electrons and holes under illumination [80]. Copyright 2017, American Chemical Society.

Figure 3 (a) Top view SEM images of perovskite with NH_4I , (b) photoluminescence spectroscopy of perovskite without and with NH_4I additive, (c) surface potential mapping of perovskite film with NH_4I , (d) schematic energy band diagram for the generation of surface photo-voltage, (e, f) carrier concentration distribution images of perovskite film without and with NH_4I [91]. Copyright 2017, WILEY-VCH.

unveiling energy band bending induced by defects but also gaining surface potential under different illumination conditions by means of measured surface work function [70,86,87]. The photoluminescence (PL) spectrum has been proposed to analyze the crystal quality and recombination process. But the spatially resolved imaging cannot be acquired by the above methods [88]. Although the fluorescence microscopy could obtain the spatially resolved PL information, the perovskite materials tend to degradation. Compared with electrochemical and optical measurements, KPFM is a non-destructive and non-contact method which can avoid the bulk recombination under any reasonable ambient conditions [89–92].

The surface defects of perovskite films can be studied in the dark or under illumination, by applying KPFM measurements [93]. Especially, when the trap states are spatially located at the surface, the electrons or holes are accumulated, which leads to the formation of a local space charge region-induced energy band bending in Fig. 3d [94]. The type of surface states determines the direction of the band bending. If the terminal surface states are acceptor-type causing the accumulation of electrons, there are upward band bending and electron depletion region, indicating that the surface states in perovskite materials are belonging to this type, and if the surface states are donor-type accumulating holes, down-

ward band bending and hole depletion region exists there. More surface trap states contribute to greater depletion layer region and then result in a large magnitude of the band bending. Under illumination, excess photo-generated carriers come into being and the diffusion current causes the redistribution of space charges [95]. Meanwhile, photo-generated holes could screen electrons accumulated at the surface, which reduces the built-in voltage and the degree of band bending.

The difference of surface potential of perovskite materials measured by KPFM with different light intensity is defined as surface photo-voltage (SPV), which is same as the difference of surface work function, manifesting the degree of change in band bending. The SPV is generated by the transfer and separation process of charge carriers, leading to the redistribution of surface charges under illumination [91]. Therefore, the value of SPV is related to surface states population which causes band bending. Therefore, SPV is employed to represent the density of surface states and higher SPV value means more trap states at the surface.

Controlling perovskite crystal growth and reducing defect density are two key factors for achieving solar cells with excellent performance. A NH_4I additive assisted method which simultaneously improves nucleation and crystal growth is utilized for high quality perovskite films.

In Fig. 3a, b, large grains are obvious with a high steady-state PL intensity, upon the addition of NH_4I . To investigate the surface properties of perovskite films with or without NH_4I , KPFM is applied under dark and illumination for getting surface potential and surface photo-voltage. SPVs decrease from 75 to 27 mV for pristine to the one with NH_4I , respectively (Fig. 3c) which suggests that NH_4I effectively reduces electronic trap states density near the surface of perovskite films, suppressing the recombination between the trapped electrons and free holes. Moreover, carrier concentration at the surface can also be calculated by surface potential attained from KPFM. Especially, Kelvin probe collects the two-dimensional imaging of the CPD between conductive tip and sample, and the value of CPD is $V_{\text{CPD}} = -(\Phi_{\text{tip}} - \Phi_{\text{sample}})/e = -(\Phi_{\text{tip}} - \chi + (E_{\text{F}} - E_{\text{C}}))/e$, where Φ_{tip} is the work function of the conductive tip, Φ_{sample} is the work functions of the sample, χ is the electron affinity of the sample, and E_{F} , E_{C} are the Fermi energy level and conduction band energy, respectively. According to Boltzmann approximation, the concentration of electrons in n-type semiconductors is $n = N_{\text{C}} \exp((E_{\text{F}} - E_{\text{C}})/(k_{\text{B}}T)) = N_{\text{C}} \exp((qV_{\text{CPD}} - \Phi_{\text{tip}} + \chi)/(k_{\text{B}}T))$, where n is the concentration of electrons, N_{C} is the effective density of states in the conduction band, k_{B} is the Boltzmann constant and T is the temperature [96]. Through highly-sensitive KPFM, the carrier concentration mappings of perovskite with and without NH_4I are shown in Fig. 3e, f. The V_{CPD} of NH_4I reduces from -355 to -423 mV and the carrier concentration at the surface improves from 6.73×10^{13} to $9.67 \times 10^{14} \text{ cm}^{-3}$. Therefore, with NH_4I , low surface trap states density and high carrier concentration are simultaneously demonstrated by KPFM measurements.

Band bending discrepancy near the surface of the perovskite film and the difference electronic trap states caused by hypophosphorous acid are analyzed through investigating surface work function of perovskite films under different light intensity *via* KPFM [93]. Besides, the difference of the surface work function in the dark and under illumination is also adopted to demonstrate that perovskite films with chlorobenzene treatment show low trap states and well photo-electronic properties [95]. Obviously, KPFM is considered as a promising protocol to study surface trap states in perovskite materials.

KPFM method is used to investigate the degradation process of perovskite materials by mapping the CPD and surface potential difference between grain boundaries and grains of perovskite films [97]. When perovskite films are exposed to high humidity environment, the CPD at grain boundaries becomes lower than the fresh films, which

implies that non-perovskite phase originates from grain boundaries towards grain interiors. By the bias voltage dependent measurements, the CPD between grain boundaries and grains of degraded sample takes more time to return previous value than that of fresh films. It suggests that more ionic defects exist at grain boundaries after perovskite films become decomposed. Based on the detection of the local property of the trap states in fresh films and degraded films, a post thermal treatment method (PTT) is adopted to remove chemical residues such as $\text{CH}(\text{NH}_2)_2\text{I}$, oxygen and water vapor. As a result, a more possible PbI_2 -terminated perovskite surface with lower ionic defects shows the lower CPD between grain interiors and grain boundaries. PTT-processed perovskite films with few ionic defects is beneficial to achieve high stability and efficiency of the devices.

Obviously, the SPV at the grain boundaries are enhanced with the light intensity, which indicates that the grain boundaries play an important role in separating the photo-generated carriers [98]. In terms of CPD mapping through KPFM, the prolonged thermal annealing is effective in reducing average surface potential, which contributes to the new formed PbI_2 phase [97]. Thus, the researchers confirmed that PbI_2 greatly reduced the surface recombination in the perovskite films and controlled the carrier behavior along the heterojunctions due to electronic bands at the grain boundary from downward bending to upward bending by passivating surface trap states. Furthermore, the surface potential distribution between grain boundaries and grains in mixed perovskites is more uniform than that of three-dimensional perovskite materials [99]. Benzoquinone and hydroquinone additives also play a similar role in achieving a flat surface potential distribution between grain interiors and grain boundaries [100]. It is indicated that the band bending at grain boundaries reduces and the electron states are trapped by the decrease of surface defects, which is in favor of the efficient charge-carrier separation and high performance. Therefore, KPFM is considered as an effective method to get a comprehensive and in-depth understanding of the trap states in perovskite materials.

Phase identification

In the field of material science, it is essential to accurately identify the composition at different localized regions for the further analysis. However, researchers often cannot recognize different specific phases only through conventional characterizations like optical microscopy and scanning electron microscopy (SEM). For instance, the

Figure 4 (a) Atomic crystal structure of perovskite by VESTA, (b) PL spectra of perovskite films under ambient conditions, (c) Raman spectra of perovskite crystal, (d) topography image of different regions, (e) surface potential mapping of different regions, (f) work function deconvolution for CH₃NH₃PbI₃, PbI₂, and CH₃NH₃I phases, respectively [102]. Copyright 2017, the Royal Society of Chemistry.

electron backscatter diffraction technique could obtain the microstructures and confirm the crystalline phases. But the beam-sensitive perovskites cannot withstand long-term exposure processing [101]. Although the crystalline phases can be confirmed by X-ray diffraction, the spatially resolved imaging cannot be acquired by such techniques [63]. Due to the difference between the Fermi level and the vacuum level for each phase, there are different work functions presented in different phases. By making use of divergence of work function, KPFM gives direct information on different phase identification through surface potential mapping [102–105].

For crystal and optical properties, the crystal structure and temperature dependent Raman spectra of perovskite (CH₃NH₃PbI₃) are performed (Fig. 4a–c). It is important that the atomic crystal structure is in agreement with HRTEM images and, according to the optical tests, there is degraded lead iodide on the surface due to Raman peaks around 200 cm⁻¹ under 150 K. As shown in Fig. 4d–f, the work function deconvolution is also derived from surface potential mapping through KPFM measurements for the further study of the specific electronic properties and spatial distribution in perovskite materials with some external conditions that may cause perovskite decomposition [106]. Compared with some earlier results

about perovskite work function, it can be considered that the low work function of CH₃NH₃PbI₃ with 4.00 eV work function (region 1) is due to the degradation. Meanwhile, the other two regions can be attributed to lead iodide phase and CH₃NH₃I phase, which are both the products of CH₃NH₃PbI₃ decomposition. Thus, KPFM test is employed to study the surface electronic structure of perovskite materials and the deconvolution of work function, which shows an n-type characteristic on the surface. Also, three regions with different components which include the perovskite and its degradation products are distinguished accurately. Additionally, the surface potential mapping of CH₃NH₃PbBr₃ and work function with the deconvolution by KPFM are also used to decipher electronic structure and phases [107]. Similar to CH₃NH₃PbI₃, the reduced perovskite work function implies a possible change in the spatial distribution of CH₃NH₃Br phase and PbBr₂ phase, which is consistent with the deconvolution calculation of work function. Therefore, the intrinsic electronic properties (p-type) and band structures of CH₃NH₃PbBr₃ are established by KPFM. In general, it is beneficial to further study the characteristics by the accurate phase identification of different regions in perovskite materials.

KPFM is also applied in conjunction with optical

microscopy and SEM to clearly determine the location of the phases. The distribution of lead iodide at nanoscale and its effect on the defect passivation in $(\text{CH}(\text{NH}_2)_2\text{PbI}_3)_{0.85}(\text{CH}_3\text{NH}_3\text{PbBr}_3)_{0.15}$ perovskite films are investigated through the combination of SEM, KPFM and fluorescence lifetime imaging microscopy (FLIM) [108]. Firstly, it is obvious that there are some grains with different contrast according to SEM images. Secondly, from surface potential mapping, the CPD of those different grains is smaller than that of other grains, even grain boundaries, which reveals the discrepancy of work function between grains with the different contrast. To get further insight into the defect passivation of the influence of those different grains, FLIM is used to provide insight carrier dynamics in the different regions. It can be concluded that those grains with lower CPD are lead iodide phase, and the carrier lifetime of the region with more lead iodide phase is longer than that of the phase with less lead iodide. So the above results show clear spatial distribution of lead iodide and the passivated defect states which facilitate the prolonging carrier lifetime of perovskite films. Besides, KPFM is performed for the direct observation of perovskite $(\text{CH}_3\text{NH}_3\text{PbI}_3)/\text{WS}_2$ heterostructures and the accurate identification of the location of the WS_2 phase and perovskite phase [109]. Although it is difficult to distinguish the difference between the two phases by optical microscopy and AFM topography, there is a clear boundary between the two phases *via* surface potential mapping. It is obvious that the regular regions with deeper colors can be attributed to WS_2 phase. As mentioned above, by combining perovskite topography images with surface potential mapping, KPFM measurements is a convenient and powerful technique which could be widely used for accurate phases or components identification on the basis of different work function.

Ion migration investigation

Ion migration in organic-inorganic perovskite materials is a key issue to J - V hysteresis in difference under different scan rates and scan directions [110–114]. Determining the fundamental mechanisms of ion migration and main factors is essential for understanding the intrinsic working principle of perovskite solar cells. Therefore, the reasonable regulation of ion migration is conducive for fabricating perovskite solar cells with a high stability, high performance and low hysteresis, and thus further promoting optimistic development of perovskite photoelectric devices. On one hand, KPFM is capable of detecting local potential changes caused by the ion

migration at precise nanoscale, giving the information on physical properties and photo-induced carriers. On the other hand, it is imperative to deeply investigate ion migration which is related to device stability and current-voltage hysteresis by detecting the CPD distribution [115–117]. For instance, bias dependent KPFM was used to confirm Fermi energy level shift and hysteresis induced by ion migration in perovskite films [118].

To accurately elaborate the key role of grain boundaries in mixed perovskite materials $((\text{CH}(\text{NH}_2)_2\text{PbI}_3)_{0.85}(\text{CH}_3\text{NH}_3\text{PbBr}_3)_{0.15})$, KPFM was used to detect the local surface potential redistribution caused by ion migration, which affects the performance of perovskite solar cells [119]. There is different CPD in the same region under different bias voltage (Fig. 5a). As presented in Fig. 5d, e, it is obvious that the change of CPD caused by negative bias is greater than that caused by positive bias. It could be considered that the 720 s of recovery time after the bias voltage removed is related to the ion migration. Moreover, as shown in Fig. 5b, c, compared with grain interiors, the change of CPD at grain boundaries is severe under large bias, which indicates that grain boundaries are the main channels for the ion migration. To further get insight of the effect of grain boundaries on ion migration, the CPD mapping images under different illumination are detected by KPFM. As depicted in Fig. 5f, built-in potential generated by work function difference between TiO_2 and perovskite could separate photo-generated hole-electron pairs under illumination. Meanwhile, bright and obvious outline in the CPD mapping is in good agreement with the previous result that is grain boundaries playing a critical role in ion migration. As a result of ion migration, MA and Pb vacancy appears in the valence band (p-type) and the I vacancies appear in the conduction band (n-type) representing that there is band bending near the grain boundary. Similarly, KPFM under 0–3.5 V bias voltage is to gain the CPD mapping in-turn to study the amount of extra PbI_2 affecting ion migration at grain boundaries [113]. Through getting insight of internal mechanism of operation process, low-hysteresis and high-performance devices are achieved by incorporating proper PbI_2 . Moreover, KPFM is also used to investigate the photoinduced bulk polarization [120,121]. Under illumination, the photoexcited charges exacerbate the rotation of CH_3NH_3^+ , consequently enhancing the dipolar polarization. For perovskite materials, polarization-induced fields contribute to internal field, which effectively enhances the charge separation and restrains charge recombination [122]. To clarify the role of

Figure 5 (a) Average CPD images under different bias, (b, c) topography and CPD mapping under -7 V bias voltage, (d) average CPD as a function of time after the bias voltages, (e) plot of the differences between contact potential differences within the grain interior and at the grain boundary under negative and positive bias voltage, (f) energy band diagram of perovskite/perovskite/ TiO_2 interface [115]. Copyright 2016, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

chlorine on bulk polarization, KPFM has been proposed to visualize the local surface potential change of grain boundaries and bulk in perovskite films. The incorporation of chlorine results in well-defined CPD mapping at grain boundaries and bulk, which indicates the decreased surface charged defects. While the ionic and charged defects could screen the photoinduced bulk polarization. Thus, the chlorine addition effectively enhances the photoinduced bulk polarization and further improves the performance of perovskite solar cells [123].

In addition to ion migration at grain boundaries, the ion migration at the interface of perovskite solar cells was also studied by KPFM [124,125]. According to CPD mapping of the interfaces of the perovskite layers, the J - V hysteresis resulted from the accumulated charges at the interface induced by ion migration [126]. The cross-sectional image of perovskite solar cell in Fig. 6a shows that Li ions are doped in the hole transport materials to investigate how the extrinsic ions affect the performance of perovskite solar cells [127]. The cross-sectional potentials of perovskite solar cells display obvious boundaries between the different regions, as shown in Fig. 6b, c. Under dark conditions, the positive and the negative pre-bias lead to the potential change, especially

at the perovskite/ TiO_2 interface. Fig. 6d shows the corresponding cross-sectional potential images of perovskite solar cells, which indicates the obvious potential drop at the interface. Generally speaking, high potential change is related to the efficient charge-carrier separation, in agreement with the theory that Li ions aggregated in the interface contribute to the charge separation. From current-voltage curves of perovskite solar cells with Li-free HTL and Li-doped HTL as illustrated in Fig. 6e, f, it is obvious that there is more hysteresis in perovskite solar cells with Li-doped HTL. Moreover, the influence of the ion migration in moisture on perovskite films was studied by KPFM [35]. It can be observed that small CPD difference between grain boundaries and interiors under controlled moisture conditions indicates the moisture-induced PbI_2 passivates the grain boundaries and suppresses the ion migration. As a result, the energy band bending and possible passivation of ion migration at grain boundaries eventually improve the device performance. Thus, getting a deep understanding and making a precise control of ion migration in perovskite grain boundaries and interfaces based on KPFM could suppress the hysteresis in perovskite solar cells. Surface potential measurements by KPFM, enable to gain a comprehensive

Figure 6 (a) Cross-sectional SEM image of the perovskite solar cell, (b, c) cross-sectional normalized potentials of the perovskite solar cells at positive (+1 V) and negative (-1 V) bias, (d) cross-sectional potential images of the perovskite solar cells under +1 V pre-bias and -1 V pre-bias, (e) J - V curves with Li-free HTL initially and finally, (f) J - V curves without/with Li doped HTL [119]. Copyright 2017, the Royal Society of Chemistry.

understanding of ion migration at the grain boundaries and the surface of hybrid perovskite materials.

CONCLUSIONS AND OUTLOOK

KPFM, as a non-destructive technique has exceptional functions for detecting local work function at atomic/molecular scales, offering the accurate surface information such as energy band bending, charge trapping, and surface reconstruction. In this review, the fundamental principle, working modes, instrumental parts and the development of KPFM technique are systematically demonstrated and the applications of KPFM towards the electron beam-sensitive materials are comprehensively reviewed. In particular, this review highlights the promising superiorities of KPFM on exploring the origin and nature of perovskite materials and provides the necessary information for optimizing solar cells, compared with other emerged characterization methods from some certain perspectives. Detailed summaries in terms of KPFM in perovskites range from the energy band structures identification to trap states-induced non-radiative recombination, from phase segregation-induced degradation to ion migration, which are helpful to effectively stimulate the evolution of the perovskite materials as well as the development of perovskite-based

solar energy harvesting devices in the future.

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Author contributions Kang Z and Si H contributed equally to this work. Kang Z and Si H wrote the manuscript. Zhang Y, Liao Q and Zhang Z investigated and analyzed published literatures. Shi M and Xu C summarized the application of KPFM on trap states investigation. Fan W, Ma S and Kausar A analyzed the fundamental principle and development status of KPFM. All authors discussed and provided feedback on the manuscripts structure, arguments and conclusions.

Conflict of interest The authors declare no conflict of interest.

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开尔文探针力显微镜在钙钛矿太阳能电池中的应用

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摘要 开尔文探针力显微镜在获得样品表面形貌的基础上可同时得到表面功函数, 且具有纳米级高分辨率, 是原位探究样品表面信息的有效表征手段。目前, 开尔文探针力显微镜作为一种无损检测手段, 在探测对水、氧和电子束辐射极其敏感的钙钛矿材料方面显示出独特的优势与潜力。本论文系统地介绍了开尔文探针力显微镜的基本原理和工作模式, 并深入地阐述了其在研究钙钛矿太阳能电池能带结构、载流子传输动力学、缺陷态、晶相种类和离子迁移方面的应用前景。开尔文探针力显微镜为揭示钙钛矿材料和太阳能电池的独特性能提供了新颖有效的方法。