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Perspective

Halide perovskite-based tribovoltaic effects for self-powered sensors

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With the rapid development of aerospace, the Internet of Things, wearable devices, and portable instruments, the application scenarios for sensors are expanding and requiring higher performance in terms of conversion efficiency, flexibility, and stability. However, most sensors are powered by an external power source, which hinders the construction of flexible sensors due to their rigid nature. In recent years, self-powered sensors have been realized by using triboelectric nanogenerators (TENGs) that convert mechanical energy from the environment into electrical energy [1]. Novel materials prepared by low-temperature solutions are one of the main research areas for self-powered sensors. Metal halide perovskite materials, which have excellent optical and electrical properties, are widely used in photovoltaic devices as well as TENGs. TENGs based on the piezoelectric and pyroelectric effects of halide perovskite materials have been thoroughly investigated [2]. Halide perovskite is a semiconductor material that can efficiently separate photogenerated electrons and holes by forming heterojunctions with different materials to generate direct current (DC) signals. Therefore, halide perovskite materials combine light absorption properties with piezoelectric/frictional effects and may be suitable candidates for temperature, pressure, and biomechanical self-powered sensors, as well as photodetectors.

Halide perovskite has been extensively studied in various types of self-powered sensors [3]. Sultana et al. [4] developed pyroelectric nanogenerators based on $MAPBI_3$-PVDF materials, which exhibit a reversible trend in output voltage and current in response to changes in external temperature and can be used as a self-powered temperature sensor for environmental monitoring and thermal imaging. Flexible pressure sensors based on the piezoelectric effect are considered as both powered and self-powered pressure sensors and have a wide range of applications in wearable electronics [5]. Nanogenerators based on $CsPbBr_3$, combined with polarization processes, can recognize various body movements in a self-powered manner with potential physiological sensing capabilities. Furthermore, combined with frictional electrical effects and photovoltaic properties, they also exhibit photostimulation responses without external power supply units and can serve as self-powered photodetectors [6,7]. Although halide perovskite self-powered sensors based on the triboelectric effects adopt a contact separation mode that directly generates alternating current by coupling contact electrification and electrostatic induction, most electronic devices require DC power supply. Therefore, a rectifier is needed to obtain DC power to drive electronic devices. This not only reduces energy conversion efficiency and increases device size, but also significantly limits the portability, miniaturization, and practical application of self-powered sensors.

DC nanogenerators based on the tribovoltaic effect are an emerging energy technology that can form Schottky and PN junctions via the contact of two materials with different work functions. Due to the directional carrier transfer between materials, DC can be generated directly through the Schottky and PN junction [8]. New structures and more suitable materials are being developed to achieve higher DC output and a wider range of applications for self-powered sensors. The invention of the Schottky junction has been utilized in rectifier circuits, sensors, and other applications [9]. Domestic and foreign scholars have observed differences in the output of DC and power generation characteristics from conventional TENGs when using semiconductor materials to study TENGs. In 2019, Wang et al. [10] first predicted and proposed the tribovoltaic effect. In 2020, Zhang's research team [11] experimentally verified this phenomenon and defined the tribovoltaic effect as the DC generation by friction between a metal/semiconductor and another semiconductor at the interface. When the two materials come into contact, interfacial electron transfer and interatomic bonding release energy and excite electron-hole pairs in the semiconductor. Subsequently, the electron-hole pairs separate under the action of the electric field built into the heterojunction, and the electrons and holes flow to different materials, forming a stable DC output. According to the principle of the tribovoltaic effect, the excitation efficiency of the electron-hole pairs strongly depends on the mutual bonding between semiconductors and the surface state density of the semiconductor. Although static perovskite PN junctions have been extensively studied and developed in photovoltaics, dynamic perovskite heterojunction energy harvesting devices have rarely been implemented. In this context, recent advances in self-powered sensors for halide perovskite materials are summarized and discussed.

Self-powered sensors based on the tribovoltaic effect have the potential to sense temperature, light, and pressure. The mechanism

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of operation is that frictional mechanical energy excites dynamic electrons on the metal side and electron-hole pairs on the semiconductor side. Under the built-in electric field, these charges separate, forming a continuous current in the loop. In a dynamic metal/semiconductor Schottky junction, the drift current and diffusion current are in a non-equilibrium state, and the bounce and acceleration of carriers at the interface between the metal and the semiconductor can generate an electrical output signal. This converts the mechanical energy generated by the relative motion of the metal and the semiconductor into a DC electrical signal. However, the theory of semiconductor DC TENGs based on the tribovoltaic effect is still not clear enough for different samples, and the output voltage and power of semiconductor TENGs are generally low, which limits their application prospects significantly. The band gap of perovskite can be adjusted by the composition, and selecting perovskite with suitable components can form Schottky and PN junctions of high quality with metal and semiconductor materials. This facilitates the development of metal/semiconductor Schottky and perovskite/semiconductor DC generators with high performance, thereby improving the performance of self-powered sensors and expanding their application prospects.

Hao et al. [12] developed a current density perovskite dynamic Schottky diode DC generator for optoelectronic-mechanical electron synergistic co-collection. By utilizing the interaction between bouncing electrons generated by mechanical energy and photogenerated carriers, they demonstrated the first DC generator with the synergistic collection of optical energy and mechanical energy from perovskite Schottky junctions. They have also created a flexible DC generator based on aluminum/perovskite/polyethylene terephthalate (PET) films, making use of the perovskite film's flexibility and lightweight properties. The generator maintained stable and excellent performance even under 120° bending, demonstrating its potential in the field of flexible sensors (Fig. 1a). To enhance the electron transfer to the metal in the perovskite film and amplify the interfacial electric field, the researchers have modulated the work function of the metal and adjusted the height of the energy level barrier of the Schottky junction. This has not only increased the charge density on the electrode but also impeded the diffusion of induced charges to the perovskite film. It is worth noting that in order to design effective perovskite DC generators, a deep understanding of electron generation and transport processes is crucial. Hence, studying the physical mechanisms involved serves as a vital guide in realizing self-powered sensors based on halide perovskite technology.

The theory of dynamic Schottky generators involves a unique physical mechanism, wherein Schottky junctions are dynamically generated and disappear as the metal and semiconductor move relative to each other. This process breaks the balance between drift and diffusion currents in the static Schottky junction region. Consequently, under specific alignment conditions of the Fermi energy levels, diffused electrons and holes are redirected back to the metal and semiconductor, respectively, due to the built-in electric field, resulting in an electrical signal output. When the work function of the metal is smaller than that of the perovskite, the electrons in the metal are transferred to the perovskite, causing the conduction and valence bands to bend downwards at the interface, thus establishing a built-in electric field. With the relative motion of the metal and perovskite, the metal/perovskite Schottky junctions are dynamically generated and disappear, causing diffused electrons and holes to bounce to the metal and perovskite under the action of the built-in electric field. The perovskite material possesses several advantages, such as a broad spectral range and a high optical absorption coefficient, resulting in the generation of a large number of photogenerated carriers when exposed to light. The dynamic generation and disappearance of depletion layers in dynamic metal/perovskite Schottky junctions provide an opportunity for the separation of photogenerated carriers subject to the tribovoltaic effect and photovoltaic effect (tribo-photovoltaic effect) coupling. Both friction and light excite electron-hole pairs, thereby simultaneously converting optical and mechanical

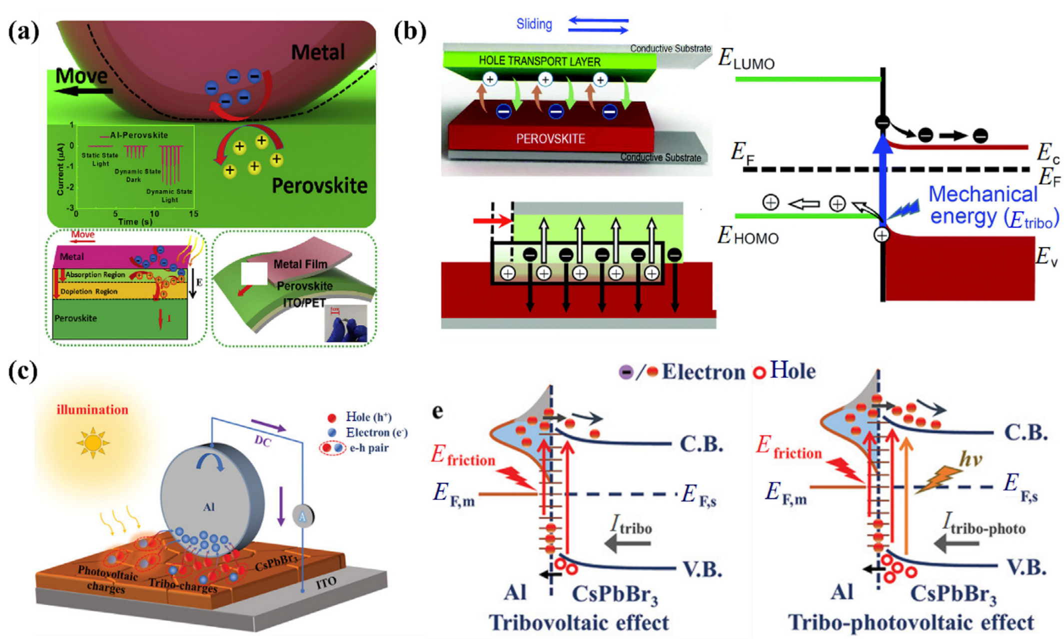

Fig. 1. (Color online) (a) Schematic illustration carrier kinetics based on a dynamic metal/perovskite schottky junction under different environments and 3D diagram of the flexible generator made of Al film/perovskite on ITO/PET. Reprinted with permission from Ref. [12], Copyright © 2019 Elsevier. (b) Schematic illustration of the dynamic perovskite/hole transport layer (HTL) heterojunction device and free charge generation by triboelectric effects and the directional charge transfer by mechanical energy (triboelectric potential). Reprinted with permission from Ref. [13], Copyright © 2021 The Royal Society of Chemistry. (c) Schematic diagram of the Al/$CsPbBr_3$ system (a rolling-mode DC-TENGs) under sunlight and band structure based on tribovoltaic effect and tribe-photovoltaic effect in dark environments and under light illumination, respectively. Reprinted with permission from Ref. [14], Copyright © 2022 Wiley-VCH.

energy into DC electrical energy, exhibiting a nonlinear light-enhancing effect. This nonlinear light-enhancing effect originates from the interaction between the bouncing carriers and photogenerated carriers generated by mechanical energy in dynamic Schottky junctions, providing a theoretical basis for the synergistic collection of optical and mechanical energy. However, further theoretical and experimental investigations are required to comprehensively understand the mechanisms underlying perovskite TENG under light conditions.

Perovskites can form not only Schottky junctions with metals to generate DC but also heterojunctions with different semiconductor materials to output DC signals. Unlike photovoltaic devices that generate electricity through photoexcitation, Ma et al. [13] demonstrated the generation of DC at dynamic perovskite/transport layer heterojunctions via triboelectric electrification. The output performance of the dynamic perovskite heterojunction device depends firstly on the carrier concentration of the perovskite material (Fig. 1b), where a high carrier concentration is beneficial to increasing the current. Secondly, the energy level of the perovskite and its contact material should be matched, and the suitable energy band position and band gap are critical for carrier separation and transfer, which suppresses the multiple compounding of carriers to a certain extent. Lastly, the voltage output performance of the DC is determined by the work function between the perovskite and the different materials used. However, it is important to note that the triboelectric effect at the interface governs the carrier generation and separation process, while the band energy level has minimal impact on controlling the voltage and current performance. This understanding provides a more theoretical foundation and yields practical solutions for the realization of self-powered sensors.

The stable output of perovskite devices holds great research significance for the development of self-powered sensors. The majority of research on the perovskite tribovoltaic effect-based DC devices involves sliding structures. Although these studies have advanced the application of perovskite materials in DC-TENGs, the mass loss and heat loss experienced in sliding structures can directly impact the stable output of the TENGs. To address this issue, Yuan et al. [14] constructed rolling-structured Al/$CsPbBr_3$ Schottky junctions using all-inorganic perovskite to prepare DC-TENGs capable of harvesting mechanical and solar energy. It is noteworthy that the TENGs show no significant degradation in output performance over 10 min of continuous operation. The Al/$CsPbBr_3$ Schottky junction depletion layer will appear and disappear dynamically at the front and back ends during the rolling process, which breaks the balance between the drift current and the diffusion current (Fig. 1c). The design of the rolling structure provides more opportunities for electron-hole separation than the sliding structure. Furthermore, the nonlinear light-enhancing effect of the perovskite DC generators enables the synergistic harvesting of optical and mechanical energy. The generators exhibit similar light-induced piezoelectric output changes during light OFF/ON, highlighting their potential to autonomously detect ambient light.

Compared to conventional semiconductors such as Si and GaAs, generators based on dynamic metal/perovskite Schottky junctions exhibit higher current enhancement under illumination. This can be attributed to the perovskite film's wide absorption range in the UV–Vis spectrum, which allows efficient absorption of incident light and generates an increased number of photogenerated carriers in the junction region located on the surface of the perovskite film. These light-generated electrons and junction region holes can be immediately scattered and accelerated by the bound-back carriers of the dynamic Schottky junction, resulting in an enhanced output current. The synergistic collection of light and mechanical energy enables perovskite TENGs to not only function as self-powered photodetectors for detecting light intensity and type but also as self-powered pressure and temperature sensors for sensing changes in the external environment. This makes them suitable for applications in wearable technology, environmental monitoring, and biomedical signal detection. Additionally, exploring the use of halide perovskite materials in multi-mode self-powered sensing devices presents a promising direction for future research to improve the detection capabilities of these sensors in various external environments.

Although research has demonstrated that the potential use of halide perovskite materials in self-powered DC nanogenerator sensors, there are still significant challenges that hinder their further development and application in this field. These challenges include the rapid annihilation of frictional charges and dissipation of composite inductive charges. The key to improving the performance of perovskite DC nanogenerators lies in increasing the frictional charge density and reducing the compounding of induced charges. To achieve this, a comprehensive investigation of the carrier transport process at the material interface is necessary, which includes studying carrier transport and compounding at the heterojunction interface. Furthermore, the stability and toxicity of these materials pose additional concerns. The presence of lead in perovskite, a toxic element, can cause environmental pollution. Moreover, halide perovskite materials tend to decompose when exposed to water, light, oxygen, electric fields, heat, and other factors, which significantly impacts the device's stability. To address these issues, optimization techniques such as surface passivation, composition tuning, and polymer composites need to be explored to improve the air stability and environmental friendliness of halide perovskite materials. Additionally, the wear and sensitivity of the DC-TENGs are also important considerations. The effective charge density of DC-TENGs during operation heavily depends on the surface contact force due to the absence of a charge accumulation process. High surface contact forces result in significant mechanical wear, leading to the rapid decay of device current density and making it challenging to achieve long-term high output.

Therefore, interface optimization is necessary, which may involve introducing buffer layers with a suitable energy band structure to improve the energy band mismatch between interfaces, carrier compounding, and mechanical wear [15]. Finally, the structure of the device greatly affects the energy conversion efficiency and device output performance. Continuous improvement and optimization of the device structure are pivotal in advancing the integration and miniaturization of self-powered energy sensors.

Conflict of interest

The authors declare that they have no conflict of interest.

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