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VIEW & PERSPECTIVE

Potential development of all-inorganic perovskites

A recent review [19] provides detailed information on the synthesis, optical properties, applications and potential development of all-inorganic metal halide nanostructured perovskites.

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The energy consumption is increasing rapidly with the continuous development of human society. Currently, global energy still mainly depends on fossil fuels. As awareness of the negative impact on the environment of burning fossil fuels, much attention has put on exploring clean and renewable energy. The solar energy has got the limitless foreground as a kind of renewable energy and photovoltaic devices can convert solar energy into electricity directly. The share of photovoltaic in renewable power generation is expected to reach 21.8% in 2030 [Fig. 1(a)] [1]. In the last two years, China is the world's largest photovoltaic market even though photovoltaic installed capacity has dropped [Fig. 1(b)] [2]. Crystalline silicon based photoelectric devices have dominated the photovoltaic market due to silicon is friendly to the environment and has abundant raw materials supplying [3, 4]. However, the silicon crystals are manufactured under high temperature and energy processing costs expensive. It is necessary to improve the efficiency and reduce the cost to reach the 2030 target.

As a challenger, perovskites have become one of the hottest topics in photovoltaic research in recent years because of the cheap and simple fabrication process, especially with outstanding optoelectronic properties including large optical absorption coefficient and long carrier diffusion lengths, which makes them efficient at absorbing light and transporting charges. The power conversion efficiency of organic-inorganic perovskites solar cells has increased from 3.8% [5] to 25.5% [6] in recent ten years, which is comparable to crystalline silicon devices. The tandem devices combining silicon and perovskites has achieved efficiency of 29.15% [6]. Moreover, as excellent optoelectrical materials, perovskites have demonstrated potential applications in light emitting diodes [7–9] because of near-unity photoluminescence quantum yields; photodetectors [10–12] operating spanning the gamma rays and near infrared spectral regions attribute to high carrier mobilities and high absorptivity of hard radiation by the heavy atoms; and optically pumped lasing [13–15] on account of large optical gain. Usually, the presence of organic groups in perovskites is extremely sensitive to thermal and moisture, which seriously affects its long-term stability. Therefore, the all-inorganic cesium halide perovskites using Cs^+ substituting organic cations are focused more and more by researchers to improve the stability. All-inorganic cesium metal perovskites have the formula $CsBX_3$, in which B is metal cation (Pb^{2+} or Sn^{2+}, etc.), X is halide ion of Cl^-, Br^-, I^- or their mixture. Besides, new forms of inorganic perovskites, such as Cs_2AgBiX_6, $Cs_3Sb_2X_9$ and other analogues, have been explored the optoelectrical characteristic in recent years.

The solution-processing is a common approach to fabricate all-inorganic perovskites materials. They could be synthesized from solution on various substrates by using readily available manufacturing techniques, including doctor-blade coating, inkjet printing and spray-coating. What's more, the optoelectronic properties can be tailored though compositional modulations. The various inorganic perovskites with controlled morphology, size, thickness and purity exhibit anisotropic optoelectronic properties, which have shown unique applications in linearly polarized photodetector, liquid crystal display and biomedical imaging devices. In 2018, Zhou *et al.* used one-step self-assembly solution methods to grow β-$CsPbI_3$ nanowires array on both of rigid and flexible tilt substrates and the photocurrent anisotropy ratio of the fabricated linear polarization photodetector reached 2.68 [16]. Most recently, Yang and co-workers reported 3D printing methods to achieve precise control of local composition and orientation of $CsPbX_3$ nanowires. The nanocomposite devices exhibit highly polarized absorption and emission properties. Application in information storage and encryption, mechano-optical sensing, and optical displays have been exhibited based on the nanocomposite devices [17]. Besides, the template-assisted growth is also an efficient way to fabricate anisotropic perovskites nanowires, which needs to prepare the nanopillar structured template firstly, the perovskites were then synthesized by solution or chemical vapor deposition (CVD) methods. Wang *et al.* reported a CVD growth of high-quality $CsPbX_3$ mi-

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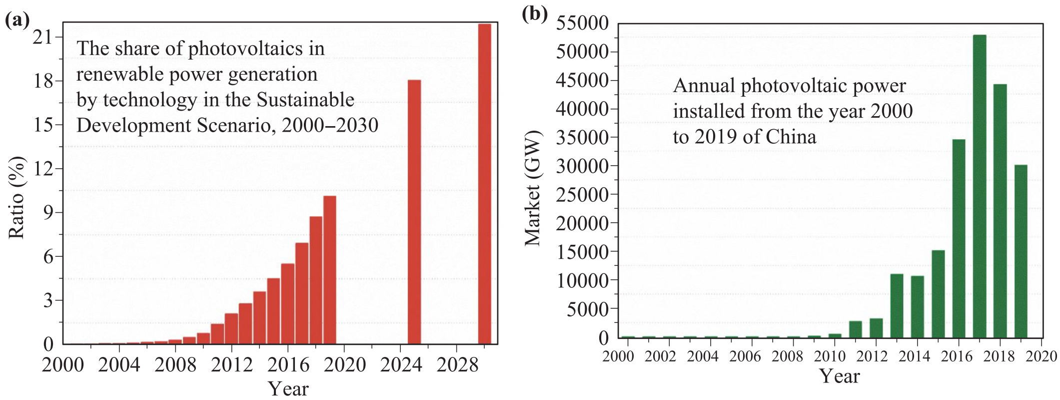

Fig. 1 **(a)** The ratio of photovoltaics in renewable power generation by technology in the sustainable development scenario, 2000–2030. **(b)** The photovoltaic development of China.

croplatelets on various substrates with tunable compositions. The as-fabricated squared platelet structure with a smooth surface can act as an excellent optical whispering gallery mode cavity to realize laser emission at room temperature [18]. In addition to the above, there are many different approaches, growth conditions and interface engineering for synthesizing all-inorganic perovskites materials, a more detailed summary is indicated in Cao's recent review [19].

More and more researchers have been drawn to the all-inorganic perovskites solar cells due to their improving stability, and the power conversion efficiency of $CsPbI_3$ based solar cell has increased from 2.9% [20] to 20.37% [21], which is slightly lower than that of organic-inorganic halide perovskites solar cells. Different temperature and experimental conditions for preparing $CsPbI_3$ would result in various crystal phases. The photoactive phase ("black phase") of $CsPbI_3$ with outstanding photoelectrical characteristic and narrow bandgap of 1.73 eV is suitable for perovskite solar cells. Unfortunately, the black phase is unstable and spontaneously transforms into an unfavorable non-perovskite structure ("yellow phase") at room temperatures (lower than 315 °C). At the same time, low open-circuit voltage (V_{OC}) will seriously reduce the efficiency limit. Consequently, many strategies have been mentioned to improve the thermal and structural stability of crystal phases and power conversion efficiency. Recently, You *et al.* claimed using long chain phenylethylammonium (PEA) and lead acetate ($Pb(OAc)_2$) as precursor to stabilize the black phase (γ-$CsPbI_3$) in 2D perovskite film and come true retaining 94% of its initial efficiency after 2000 hours in dry air box with the humidity of 5%–10%. Especially, the device reached a stable power conversion efficiency output of ~17% and highly reproducible V_{OC} of 1.33 V, along with the V_{OC} deficit of 0.38 V [22]. Seok and co-workers fabricated $CsPbI_3$ based perovskite solar cells with an excellent efficiency ~20.37% by combining optimal sequential dripping of a methylammonium chloride (MACl) solution (SDMS) and octylammonium iodides (OAI) passivation to improve the surface morphology [21]. $CsPbI_2Br$ has been extensively researched because of its balance between the phase stability and the suitable bandgap of 1.92 eV. Miyasaka *et al.* utilized $SnCl_2$ solution aging method to fabricate $CsPbI_2Br$ based solar cells with the champion V_{OC} of 1.43 V and the V_{OC} deficit was reduced to <0.50 V, which may be potential for fabricating tandem solar cells [23]. In addition, numerous all-inorganic perovskites solar cells have been explored by means of interface engineering, compositional modulation, synthesis methods, and defect passivation to improve the performance, as indicated in Zhang's [24] and Yip's [25] recent reviews.

Nowadays, thousands of researchers are involved worldwide in the development of all-inorganic perovskites meterials. These great efforts and the excellent material properties might eventually lead to commercial application of the inorganic pervskite optoelectronic devices. However, there are major obstacles need to be solved, as illustrated in Fig. 2. First, the stability and efficiency of the device should be further improved though much progress has been made. At the same time, low cost should be maintained. Optimization of growth process,

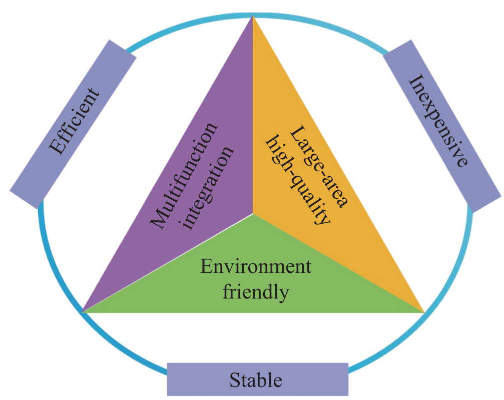

Fig. 2 Potential improvement of all-inorganic perovskites.

alternative designs, interface passivation, exploration of low-dimensional materials, encapsulation, and combination with other materials could lead to breakthroughs in the near future. Second, the toxicity of lead is also influence on its development and that has become a trend to develop lead-free perovskites such as $CsSnX_3$, $CsGeX_3$, Cs_2AgBiX_6, $Cs_3Sb_2X_9$ and so on. Nevertheless, the performance of these devices is especially poor and needs to be further improved. Thirdly, the defects and disunity morphology will become more obvious as the area increasing of perovskites film, which makes it difficult to guarantee the uniform electronic properties. Therefore, it is necessary to explore new technology to produce large-area, high-quality all-inorganic perovskites film. Last but not least, integrate perovskites devices into special application systems is worth promoting. Recently, Gu *et al.* presented biomimetic eye with a hemispherical perovskite nanowire array retina integrated with other electrical system [26], which will inspire more research and development of perovskite device in new area and pave the road to commercialization. In Cao's recent review [19], they provides detailed information on the synthesis, optical properties, applications and potential development of all-inorganic perovskites, which help us full-scale and deep understanding of them.

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