Chapter

Introductory Chapter: Perovskite Materials and Advanced Applications

Xiangshun Geng, He Tian and Tian-Ling Ren

1. Perovskite structure and synthesis

Perovskite is considered one of the most promising materials of the twenty-first century. In the past few decades, the perovskite has attracted broad attention and made great progress in energy storage, pollutant degradation as well as optoelectronic devices due to its superior photoelectric and catalytic properties. All materials with ABX_3 structure are collectively referred to as perovskite materials, which can be simply divided into inorganic perovskite and organic-inorganic hybrid perovskite. The tolerance factor is usually used to indicate the structure of perovskite. Each ion radius in perovskite oxide should satisfy the following equation: $t = ((r_A + r_O))/(\sqrt{2}(r_B + r_O))$, where r_O, r_A, and r_B are the radii of respective ions A, B, and oxygen elements. So far, various perovskites, such as Ba_2XOsO_6 (X = Mg, Zn, Cd), $Cs_2AgBiBr_6$, and $CH_3NH_3PbX_3$ (X = Cl, Br, I), have been synthesized and used in different fields. For example, perovskite oxides play a pivotal role in half-metallic ferromagnetic, spintronic applications, energy storage, and pollutant degradation, while the halide perovskite is used for LEDs and photodetectors. Currently, diverse preparation methods have been developed for the synthesis of perovskite with different dimensions. For instance, solid phase synthesis method and sol-gel method are used for synthesizing perovskite oxide and hydrothermal method for halide perovskite.

1.1 Solid phase synthesis

Solid phase synthesis is a traditional preparation to obtain perovskite oxides by evenly mixing two or more kinds of metal salts and pressing them into sheets. After calcining at a certain temperature, this material can be acquired by grinding calcined sample. To study its magnetism, Yuan et al. prepared the perovskite oxide $Y_{1-x}Gd_xFeO_3$ ($0 \le x \le 1$) with good crystal structure by solid phase method [1]. This preparation process has the advantages of simple production process and low cost, and as-prepared materials have high mechanical strength.

1.2 Sol-gel method

Organometallic compounds or inorganic metal salts as precursors are hydrolyzed or alcoholized to form sol and are finally condensed to form gel. After heat treatment, the required oxide powder is obtained. The commonly used gels include ethanol, ammonia, polyvinyl alcohol, citric acid, etc. Taguchi et al. synthesized $LaCoO_3$ with small particle size by using ethylene glycol and citric acid as gel [2]. Besides, the effects of different calcination temperatures on the properties of materials were also studied by Toro et al. [3].

1.3 Hydro-thermal synthesis

Using an aqueous solution as the reaction medium, perovskite crystals were precipitated in the reaction vessel under high temperature and pressure. Wang et al. have prepared the perovskite oxide of $LaCrO_3$, $La_{0.9}Sr_{0.1}CrO_3$, and $La_{0.8}Sr_{0.2}CrO_3$, in which the grain size is between 1 and 2 μm [4]. The crystallinity, particle size, and morphology of materials can be controlled by hydrothermal process and prepare ultra-fine, less agglomerated, and grow single-crystal spherical core-shell perovskite materials.

1.4 Vapor deposition

This technique mainly uses one or several gas phase compounds or elemental materials containing thin film elements to produce thin films by chemical reactions on the substrate surface. Liu et al. have reported the first vapor-deposited perovskite films through dual-source evaporate $PbCl_2$ and CH_3NH_3I on the FTO substrates [5]. Later, smooth and highly crystalline perovskite thin films were prepared by pulsed laser deposition [6]. Large amount of researches have revealed that the quality has a great influence on the precursor ratio control and deposition rate. Besides, chemical vapor deposition, as a general method, is also used to synthesize one-dimensional nanowires [7, 8] and two-dimensional microplatelets [9].

1.5 Solution-chemistry approaches

Solution-chemistry approaches, such as spin-coating, anti-solvent crystallization, inverse temperature crystallization, are low-cost and facile processes for preparing perovskite films and high-quality crystals. There are two strategies of one- and two-step methods about the spin-coating method. In the one-step method, perovskite precursor solution was directly applied to the substrate surface and formed perovskite film after annealing treatment. However, the main challenge of volume shrinkage has a great impact on the quality of the film. Thus, two-step

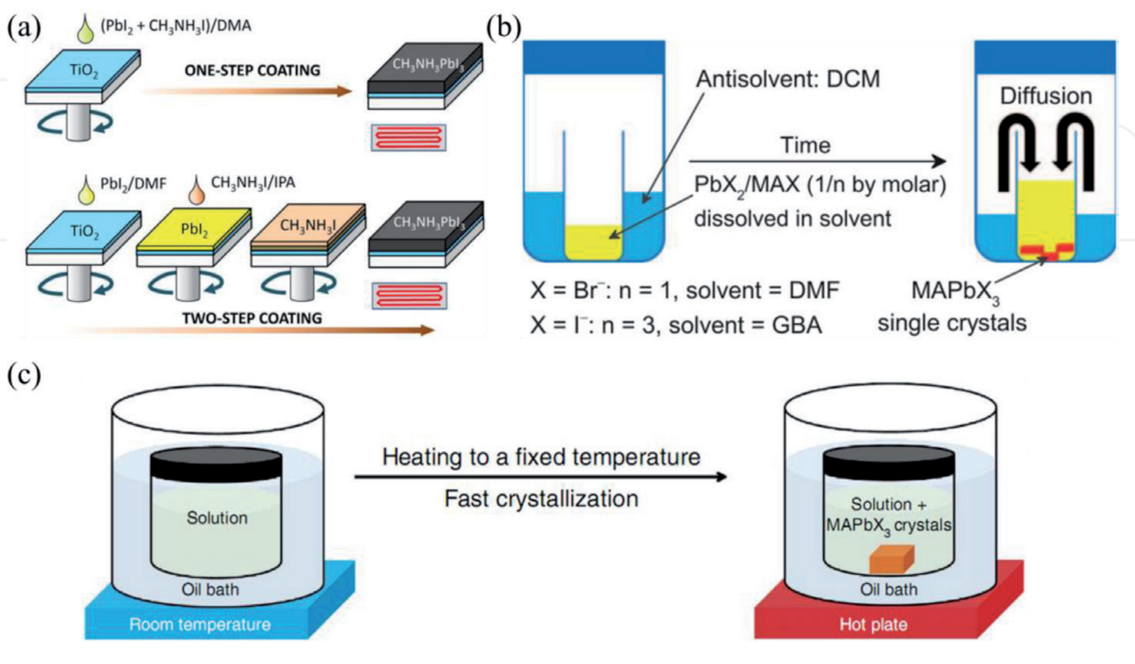

Figure 1.
(a) The illustration of spin-coating method, (b) anti-solvent crystallization, and (c) inverse temperature crystallization for preparing perovskite materials.

method is development for the preparation of uniform perovskite films, which could reduce this disadvantage to some extent. For synthesizing bulk crystals, Shi et al. proposed anti-solvent process to prepare low trap-state density and long carrier diffusion $CH_3NH_3PbBr_3$ single crystals [10]. After that, two-inch-sized perovskite $CH_3NH_3PbX_3$ (X = Cl, Br, I) crystals were prepared by inverse temperature crystallization [11]. **Figure 1** shows the schematic diagram of various solution-chemistry approaches [10, 12, 13].

2. Perovskites for devices

Perovskite has been widely used in many fields due to the great progress in material and device preparation technology. Up to date, there are numerous perovskite applications including degradation of organic pollutants, optoelectronic devices, and memory devices. Next, we will discuss perovskite applications separately.

2.1 Perovskite for catalyst

With the enhancement of environmental awareness, the construction of sustainable development society has become the current consensus. Due to the excellent catalytic properties, perovskite has a great application prospect in the degradation of organic pollutants and the acquisition of clean energy. It is well known that NO_x is one of the main causes of air pollution. Several studies were carried out to achieve NO_x-to-N_2 conversion by using perovskite-based catalysts. Furthermore, perovskite also shows exotic catalytic properties to other harmful gases, such as CO [14] and SO_2 [15], which effectively reducing pollutants in the environment. To effectively manage clean energy, previous work mainly focused on perovskite-based solid oxide fuel cell and water electrolysis.

2.2 Perovskite for optoelectronics

2.2.1 Solar cells

Perovskites are considered to be the most promising candidates for solar cells due to their excellent diffusion length (more than 1 μm), low preparation temperature, low cost, and high efficiency. In 2009, Kojima et al. first prepared perovskite solar cells [16], which is an important step for the development of solar cells. Later, Burschka et al. fabricated the solar cells by two-step continuous deposition method, and the photovoltaic conversion efficiency was increased to 15% [17]. And then, the performance was improved by changing device structure and optimizing carrier transport layer [18]. So far, the efficiency of perovskite solar cells has exceeded 22% [19]. The huge development of perovskite solar cells will provide the possibility for its commercialization.

2.2.2 Photodetectors

Photodetectors, which could convert incident light into electrical signal, are very important optoelectronic devices for optical communications, homeland security, and environmental monitoring. Many works have reported that perovskite-based photodetectors have the abilities to sense the spectra from deep-UV to visible and NIR [20, 21] and even to X-ray or γ ray [22, 23]. Efforts have been devoted to improve the device performance. For example, wide spectrum detection from

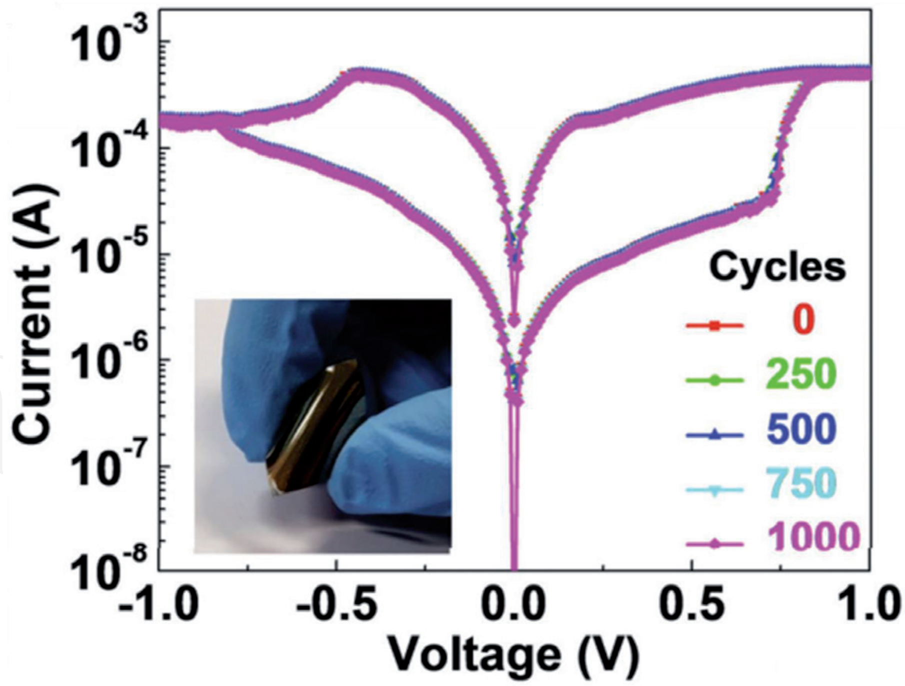

Figure 2.
Resistive switching characteristics and the photograph of the flexible device.

visible to near-infrared was realized by adjusting perovskite components [24]. The passivation of graphene makes the detectable light intensity of the device down to 1 pW/cm^2 [25]. Recently, flexible photodetectors and detector arrays have been prepared. Therefore, perovskite photodetectors are developing toward the direction of high performance and practicality.

2.3 Memory devices

Resistive memory (RRAM) is a non-volatile memory based on reversible conversion between high- and low-resistive states under the action of applied electric field. Zhang et al. were the first to demonstrate a 64-bit RRAM array utilizing perovskite oxide $Pr_{0.7}Ca_{0.3}MnO_3$ materials by a 500 nm CMOS process [26]. This RRAM array has a high/low resistance ratio larger than 1000. After that, multilayer-graphene transparent conductive electrodes were employed for flexible perovskite RRAMs [27]. Resistive switching characteristics and the photograph of the flexible device are shown in **Figure 2**. A typical structure of resistive random-access memories is a metal/insulator/metal (MIM) stack. The applied bias can adjust the operating state of the device at will, in which high resistance state (HRS) and low resistance state (LRS) can be formed. Conductive filament and uniform modes are currently recognized resistance conversion mechanisms. As the most common mechanism, ion migration and metal-insulator transition are considered to be the main cause of the filament mode. Besides, uniform resistance switching mainly includes the carrier trapping/detrapping and the ferroelectric polarization.

Author details

Xiangshun Geng, He Tian* and Tian-Ling Ren*
Institute of Microelectronics and Beijing National Research Center for Information Science and Technology (BNRist), Tsinghua University, Beijing, China

*Address all correspondence to: tianhe88@tsinghua.edu.cn
and rentl@tsinghua.edu.cn

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