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News & Views

Fabrication of stable organometallic halide perovskite NWs based optoelectronic devices

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Organometallic halide perovskite materials have triggered global attention in recent years due to their exciting and optimistic high performance energy conversion properties (high luminescence efficiency and tremendous optical absorption ability [1,2]). These interesting photovoltaic properties together make them a promising candidate for high performance optoelectronic devices (Solar cells, Photodetectors, Image sensors and Light emitting diodes etc.) and switching from CdTe devices [3]. Despite of outstanding and stunning energy conversion abilities of organic perovskite materials, a big associated drawback with these materials is the poor stability and durability under ambient conditions. Organic perovskite is an ionic compound and destabilizes very quickly upon invasion of oxygen and water molecules [4–6]. A sequential decay process of perovskite material with oxygen and water diffusion has been explained below [7].

$$MAPbI_3(s) \xrightarrow{H_2O} PbI_2(s) + CH_3NH_3I(aq) \quad (1)$$

$$CH_3NH_3I(aq) \xrightarrow{H_2O} CH_3NH_2(aq) + HI(aq) \quad (2)$$

$$4HI(aq) + O_2(g) \longrightarrow 2I_2(s) + H_20(l) \quad (3)$$

$$2HI(aq) \longrightarrow H_2(g) + I_2(s) \quad (4)$$

These equations point out that perovskite decay process is self-sustaining and self-accelerating due to generation of water as a byproduct. Water existence triggers and propagates this decay process till complete degradation of perovskite material as demonstrated with schematic in Fig. 1. On exposure to moisture, water and oxygen diffuse quickly across the grain boundaries of perovskite polycrystalline films and cause quick degradation of material [8]. Existing literature reports have tried to tackle this issue by tuning compositional mixture of halides and encapsulation [9,10]. Encapsulation is a popular method for providing protection, however previous encapsulation reports tried to slow down this decay with encapsulation of material on top only with help of different polymers [10–13]. They did not pay heed to lateral diffusion of water molecules which may occur even with effective protection on top. Lateral encapsulation of perovskite material is as critical and important as top surface protection. It concludes that decay process can be effectively hindered or slowed down by effective top and lateral enclosure of perovskite material from water and oxygen diffusion.

A recent research from Gu et al. [14] and Waleed et al. [15] in HKUST tried to come up with a novel idea of lateral protection for perovskite material, provided by anodized alumina template as demonstrated with schematic in Fig. 1. It was discovered that stability of perovskite material ($CH_3NH_3SnI_3$ and $CH_3NH_3PbI_3$) was enhanced dramatically by lateral protection of anodized alumina. Anodized Alumina template is a suitable choice for lateral protection due to its low-cost, high melting point and easy fabrication methods.

In these works [14,15], three dimensional $CH_3NH_3PbI_3$ and $CH_3NH_3SnI_3$ perovskite nanowires (NWs) array were effectively grown from Pb/Sn metal precursor inside anodized alumina template by simple and low-cost vapor solid solid (VSS) method at 170 °C as shown in Fig. 2a. Perovskite material was grown by reaction of vaporized Methylammonium (MAI) with Pb metal clusters inside chemical vapor deposition (CVD) chamber. Growth chain follows $Pb/Sn \rightarrow PbI_2/SnI_2$ before complete conversion to $CH_3NH_3PbI_3$ and $CH_3NH_3SnI_3$. This is a two-step growth process with PbI_2/SnI_2 as intermediate products. The overall growth process for $CH_3NH_3PbI_3$ and $CH_3NH_3SnI_3$ perovskite material can be summarized by following equations [14–16].

$$Pb(s) + 3CH_3NH_3I(s) \longrightarrow CH_3NH_3PbI_3(s) + 2CH_3NH_2(g) + H_2(g) \quad (5)$$

$$Sn(s) + 3CH_3NH_3I(s) \longrightarrow CH_3NH_3SnI_3(s) + 2CH_3NH_2(g) + H_2(g) \quad (6)$$

Perovskite NWs were usually grown by evaporation of $MAPbI_3$/DMF solution in open air [17] but air moisture evolves crystal damaging, polycrystallinity and rough surfaces in NWs [4]. This method has superiority over existing NWs growth methods in terms of air moisture hindrance and guided channel growth during whole process. Due to these reasons, this growth approach provided single crystalline and smooth surfacing to these NWs grown inside template. Consequently, single crystallinity and tight physical confinement of template provide enhanced stability to these NWs as compared to perovskite materials without lateral protection.

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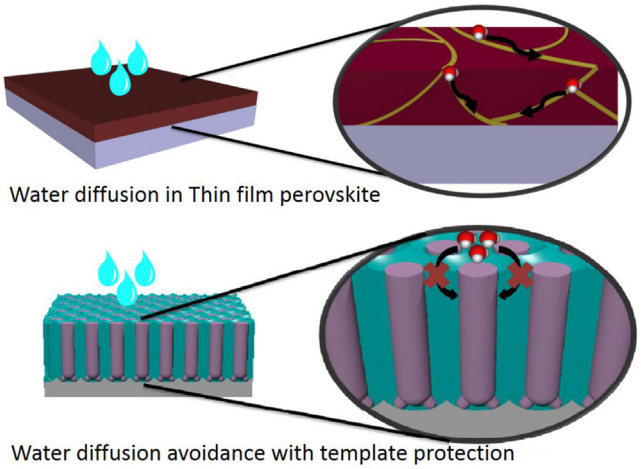

Fig. 1. (Color online) Schematic illustration of lateral protection mechanism.

Later, stability measurements based on these perovskite NWs showed that effective and tight mechanical embedding inside anodized alumina template slows down the decay process of perovskite material. Photoluminescence (PL) emission was used to quantify the decay of material. PL emission decay measurements showed that decay process of sidewall protected perovskite material declines ~840 times as compared to thin film samples with no lateral protection as shown in Fig. 2b. This splendor of stability can be associated with effective lateral protection of material from moisture and oxygen which brings a dramatic increase in stability. This stability measure can be tremendously increased further by involving encapsulation on top. PL emission measurements showed that these NWs stability improved further by adopting polymer packaging protection on top surface. PL emission remained almost same even after a week for sample with top and lateral encapsulation.

As described earlier, stability is a big hindrance in realizing long lasting and durable devices based on perovskite materials, so photodetector and image sensor devices were realized by involving these highly stable perovskite NWs inside template. High density and stability of these perovskite NWs contributes in realization of optoelectronics devices. A 1024-pixel image sensor based on $CH_3NH_3PbI_3$ was fabricated and their ability to capture still and dynamic images was well demonstrated by Gu et al. [14]. In a similar fashion, a stable photodetector device based on physically embedded $CH_3NH_3SnI_3$ NWs inside anodized template was realized by Waleed et al. [15] to demonstrate the importance of lateral protection. It was discovered that photodetector device based on these tightly embedded $CH_3NH_3SnI_3$ NWs outperformed thin film device. Light current decay of photodetector device was ~500 times slower than thin film device. This light current comparison can be understood with light current comparison curves demonstrated in Fig. 2c.

Overall, this highlighted work demonstrates for the first-time a low cost, simple, novel and well controlled guided growth of single crystalline organometallic halide perovskite NWs from chemical reaction between Pb/Sn metal precursor and MAI vapors by chemical vapor deposition (CVD). This is a non-catalytic growth mechanism which is distinctively different with inorganic NWs growth in the past. Furthermore, optical measurements results are clear evident that lateral protection is of crucial importance along with top protection of perovskite for enhancing the stability measures. Note that although performance and stability of perovskite material can be further enhanced by growing bulk single-crystal perovskite thin films, these single crystalline perovskite nanowires have advantages in terms of flexibility and they can readily be used for integrated nanoelectronics and optoelectronic devices. These reported 3-D vertical perovskite NWs have attracting properties of (1) Enhanced stability (2) single crystallinity (3) very high-density $4 \times 10^8/cm^2$ (4) periodic symmetry (5) low cost fabrication and (6) tunable geometry of NWs. These above-mentioned properties make them suitable candidates for their usage in high

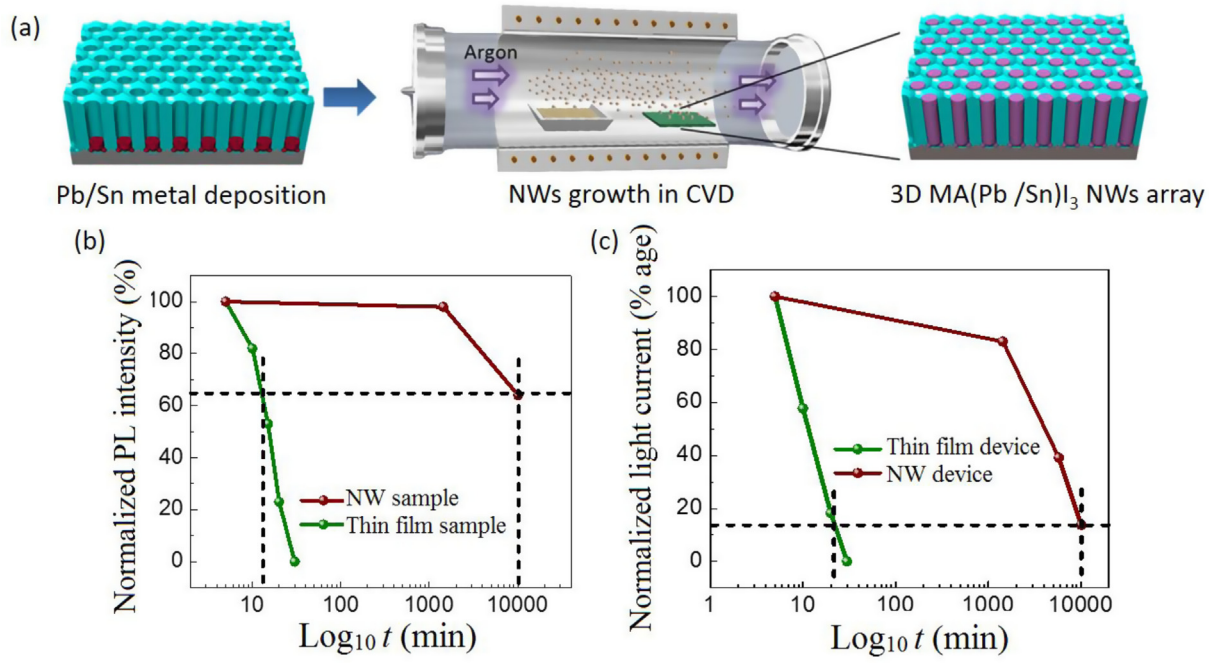

Fig. 2. (Color online) The overall growth schematic for organometallic perovskite NWs and quantified material stability improvement over polycrystalline perovskite thin film. (a) Growth schematic for 3D organometallic perovskite NWs inside CVD furnace. (b) Normalized PL intensity comparison for thin film and NWs perovskite sample. (c) Normalized light current decay comparison of lateral protected NWs and thin film photodetector devices. (Adapted from Ref. [15].)

performance and stable optoelectronic devices. As a proof concept image sensor and photodetector devices were fabricated from these NWs which showed high performance in terms of stability and reliability.

Conflict of interest

The authors declare that they have no conflict of interest.

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