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Synthesis and Properties of Perovskite/2D Material Heterostructures

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Abstract: *Organic-inorganic hybrid perovskites are one of the most extensively studied materials for diverse optoelectronic applications such as, solar cells, photodetectors, and light emitting diodes. Thus, vertically stacked heterostructures of perovskites with various materials provides new routes to achieve better device performance, increase efficiency and, expand the application areas in the perspective of optoelectronic devices. However, most of the studies on perovskites have focused on solution based deposition techniques which gives bulk thin films that are difficult to be implemented into heterostructure by conventional lithography techniques because these perovskites are soluble in most of the common solvents. Here, we show solvent and lithography-free synthesis and optical properties of vertically aligned heterostructures of perovskite and* WS_2.

Keywords: Perovskite, TMDC, Heterostructure

1. INTRODUCTION

Over the past decade, organic-inorganic hybrid perovskites have attracted great attention thanks to their exceptional properties, such as long carrier diffusion lengths, high optical absorption, strong luminescence, and bandgap tunability through chemical composition [1]. Methylammonium lead halide perovskite is a sub-class of perovskites with the chemical formula $CH_3NH_3PbX_3$, where $CH_3NH_3^+$ and Pb^{2+} are cations, and X (I^-, Br^- or Cl^-) is anion (Fig. 1) [2]. Meanwhile, monolayer transition metal dichalcogenides (TMDCs) such as WS_2 are considered to be one of most promising materials for electronic and optoelectronic applications because of their superior physical and optical properties. WS_2 shows unique band structure that depends on number of layer; while bulk WS_2 is an indirect semiconductor, monolayer WS_2 is a direct-gap semiconductor with a bang gap of ~2.0 eV. WS_2 shows strong photoluminescence (PL) in the visible range and also has excellent device performance with high on/off ratios [3].

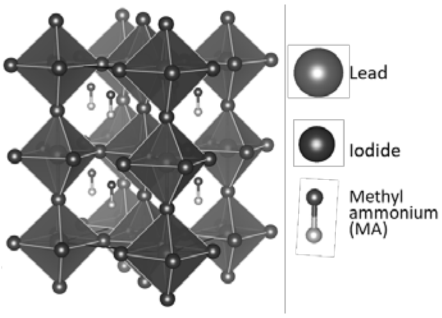

Fig. 1. Crystal model of $CH_3NH_3PbI_3$.

Considering the advantages of these two classes of materials, integration of the perovskites with TMDC materials offers a new opportunity to obtain unique properties. However, because of the vulnerability of perovskites to common solvents, conventional wet transfer processes are not applicable to create new heterostructures [4].

In this study, we demonstrate preferential vapor deposition of lead iodide (PbI_2) onto monolayer WS_2 and successive vapor-phase conversion to perovskite (methyl ammonium lead iodide ($MAPbI_3$))/WS_2 heterostructure. Preferential growth of PbI_2 via vapor deposition allowed us to obtain large area and uniform perovskite/WS_2 heterostructures which is unattainable through other methods, such as spin coating, drop casting, or mechanical exfoliation.

2. EXPERIMENTAL PROCESS

Synthesis of the monolayer WS_2 by chemical vapor deposition (CVD) on c-plane sapphire reported by our group earlier [3, 5]. Briefly, WO_3 and sulfur powders were placed in a three-zone furnace. The WO_3, sulfur, and substrates were heated at 1065 ºC, 165 ºC and 925ºC, respectively, while keeping the system under constant Ar flow at ambient pressure. For vapor-deposition of PbI_2 onto WS_2, PbI_2 powder was placed on center of a CVD furnace. As-grown WS_2 on sapphire substrate was put in the downstream. Then quartz tube was evacuated to base pressure and followed by 50 ccm of Ar gas. Temperature was gradually increased to 360ºC and deposition was carried out in 15 min. Figure 2 shows a schematic representation of the experimental setup. Afterwards, PbI_2 was converted to perovskite ($MAPbI_3$) by vapor phase intercalation of methyl ammonium at 130 ºC for 4 h under a constant Ar flow.

Optical images were taken by optical microscope (Nikon Eclipse ME600). Raman and photoluminescence (PL) spectra were measured with a Raman spectroscope (Tokyo Instruments Nanofinder 30) using a 532 nm excitation laser at low excitation power.

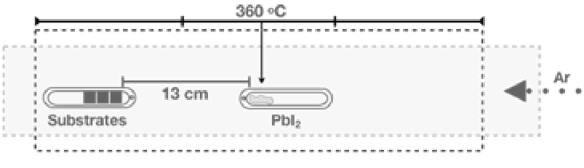

Fig. 2. Schematic representation of vapor-deposition setup.

3. RESULTS AND DISCUSSION

Figure 3a shows a schematic illustration of perovskite/WS_2 heterostructure. The optical image of perovskite with different thicknesses on WS_2 is given in Figure 3b. Layered structure of PBI_2 is noticeable on the optical image.

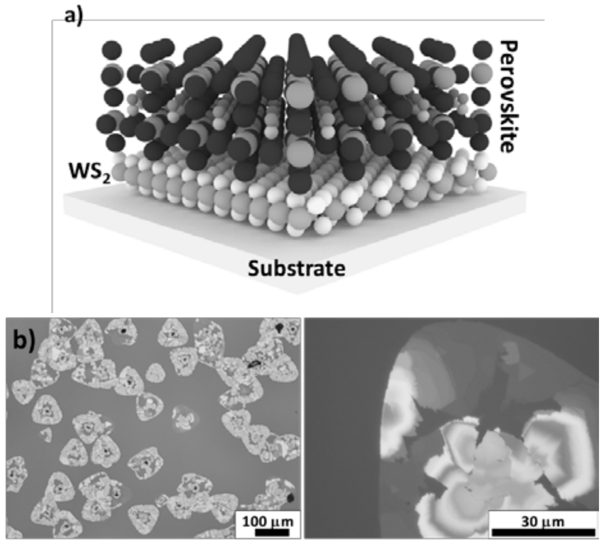

Fig. 3. a) Schematic illustration of perovskite/WS_2 heterostructure. b) Optical image of perovskite with WS_2.

Raman spectra taken from the pristine PbI_2 and perovskite on WS_2 were given in Figure 4. For PbI_2 and perovskite, the Raman peak at 73 cm^{-1} was assigned to the shearing motion between two iodide layers (Eg). The vibration at 97 cm^{-1} corresponded to the symmetric stretch (A_{1g}). On the other hand, WS_2 gave in-plane acoustic phonon mode 2LA(M) at 356 cm^{-1} and A_{1g} mode at 418 cm^{-1}. These results imply that we successfully deposited PbI_2 and converted it perovskite without damaging monolayer WS_2.

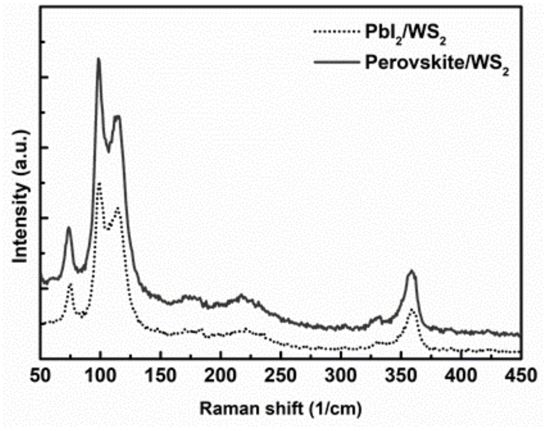

Fig. 4. Raman spectra of pristine PbI_2 and perovskite on WS_2.

Photoluminescence (PL) spectra have been taken from pristine $MAPbI_3$, pristine WS_2, and the heterostructure (Fig. 5). The thick pristine $MAPbI_3$ showed an intense PL peak at ~1.65 eV, while WS_2 showed a moderate PL peak at ~2.0 eV. In the case of the heterostructure, PL peaks from both $MAPbI_3$ and WS_2 were significantly quenched. It is known that $MAPbI_3/WS_2$ interface exhibits type-II band alignment which is desirable for photonic devices, such as solar cells, photodetectors, and light emitting diodes [6]. Considering the type-II band alignment, PL quenching can be attributed to charge transfer at the interface.

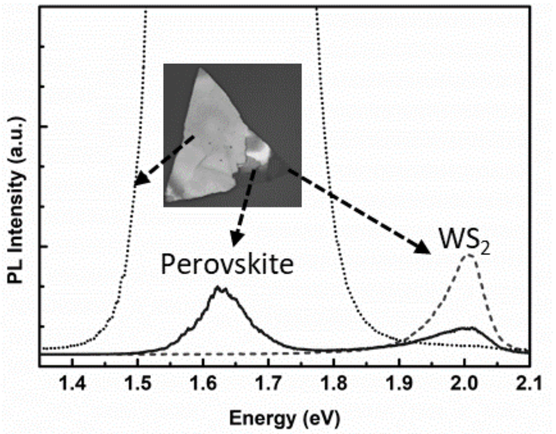

Fig. 5. PL spectra of pristine $MAPbI_3$, pristine WS_2, and the heterostructure.

Figure 6 depicts a PL mapping for perovskite on WS_2, indicating that WS_2 is fully covered with a uniform perovskite layer.

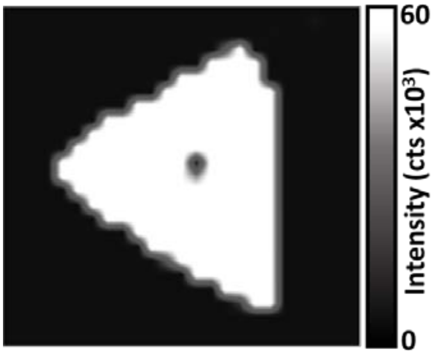

Fig. 6. PL mapping of perovskite deposited on a WS_2 grain.

4. CONCLUSIONS

Vertically stacked heterostructure of perovskite/WS_2 was achieved by vapor-deposition method without causing damage on either of the materials. Therefore, we believe that this solvent-free approach will enable new applications in optoelectronics, especially, for light diodes and photodetectors which require advanced patterning techniques.

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