Atomically thin two-dimensional materials as hole extraction layers in organolead halide perovskite photovoltaic cells

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HIGHLIGHTS

- MoS_2 and WS_2 layers were prepared by chemical vapor deposition method.
- Graphene oxide (GO) was synthesized by Hummers' method.
- MoS_2, WS_2, and GO can be applied to the hole extraction layer for perovskite solar cell.

GRAPHICAL ABSTRACT
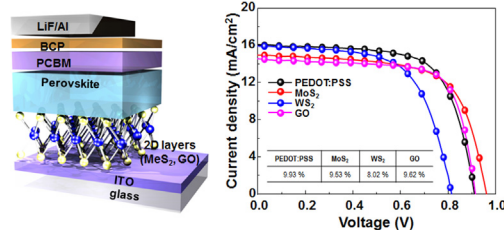
ABSTRACT

Atomically thin two-dimensional materials such as MoS_2, WS_2, and graphene oxide (GO) are used as hole extraction layers (HEL) in organolead halide perovskites solar cells (PSCs) instead of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) HEL. MoS_2 and WS_2 layers with a poly-crystalline structure were synthesized by a chemical deposition method using a uniformly spin-coated $(NH_4)MoS_4$ and $(NH_4)WS_4$ precursor solution. GO was synthesized by the oxidation of natural graphite powder using Hummers' method. The work functions of MoS_2, WS_2, and GO are measured to be 5.0, 4.95, and 5.1 eV, respectively. The X-ray diffraction spectrum indicated that the synthesized perovskite material is $CH_3NH_3PbI_{3-x}Cl_x$. The PSCs with the p-n junction structure were fabricated based on the $CH_3NH_3PbI_{3-x}Cl_x$ perovskite layer. The power conversion efficiencies of the MoS_2, WS_2, and GO-based PSCs were 9.53%, 8.02%, and 9.62%, respectively, which are comparable to those obtained from PEDOT:PSS-based devices (9.93%). These results suggest that two-dimensional materials such as MoS_2, WS_2, and GO can be promising candidates for the formation of HELs in the PSCs.

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1. Introduction

Organic photovoltaic (OPV) cells have attracted considerable attention because of their low cost, light weight, flexibility, and ease of enlargement through the roll-to-roll coating process [1,2]. Although a power conversion efficiency (PCE) of over 10% has been achieved by the OPV cells using a comprehensive material design for appropriate materials, structure optimization, and molecule engineering, it is difficult to find a breakthrough for further increasing the PCE value [3–5]. In order to overcome this difficulty, organolead halide perovskite has emerged as an exciting material in the photovoltaic research field because of its large light

absorption coefficient, high carrier mobility, and long carrier diffusion length [6–8]. The organolead halide-based photovoltaic cell was first introduced in 2009 as a sensitizer for dye-sensitized solar cells [9]. The structure of the perovskite solar cells (PSCs) has progressed from a perovskite dot deposited on TiO_2 with a PCE of 9.7% to a planar p-n junction with a PCE of 15.4%, via the meso-superstructured scaffold Al_2O_3 concept with a PCE of 10.9% and perovskite-infiltrated nanocomposite with a PCE of 15% [10]. Through the progress of the structure and the materials, the PCE value has increased to 20.1% using formamidinium lead iodide and methylammonium lead iodide as active materials for the PSCs with a planar *p-i-n* junction structure [11].

Electron and hole conductors are important in PSCs with a planar p-n junction structure to achieve outstanding device performance. The $CH_3NH_3PbI_2Cl$ or $CH_3NH_3PbI_3$ films have been reported as active materials for the PSCs owing to their long electron–hole diffusion lengths exceeding 1 μm and 100 nm, respectively [7]. Poly(3,4-ethylenedioxythiophene): poly(-styrenesulfonate) (PEDOT:PSS) and phenyl-C_{61}-butyric acid methyl ester (PCBM) are conventionally used as the *p*- and *n*-type semiconductors in the *p-n* junction PSCs, where holes are collected at the transparent conductive anode and electrons are collected at the metal cathode. Although PEDOT:PSS is one of the best *p*-type semiconductors because of its adequate energy level, excellent carrier mobility and simple solution process, it has been reported that PEDOT:PSS is not suitable for practical applications owing to its hygroscopic effect and high acidic property, which causes fast degradation of organic layers and organolead halide perovskites layer [12–14]. Furthermore, the organolead halide perovskites layer results in the dissociation of the crystal structures upon contact with the moisture in the air [15]. According to these concerns, inorganic charge transport layers have been used, such as NiO_x and CuSCN [13,14]. Therefore, the development of a hole extraction layer (HEL) instead of PEDOT:PSS is required to fabricated PSCs with high PCE and long-term stability.

Graphene oxide (GO) was used as the HEL in the OPV cells due to its high work function after surface treatment, simple fabrication process, and relative stability when exposed to air as compared with PEDOT:PSS [16]. Because of the excellent charge transport properties of the transition metal dichalcogenides (TMDs) such as MoS_2, WS_2, TaS_2, and TiS_2, two-dimensional TMDs were used as both hole and electron transport layers in the OPV cells [17]. The lone-pair electrons of the carbon and chalcogen atoms in the isolated monolayer structure of GO and TMDs enable ballistic transport, indicating improved carrier mobility [18]. Furthermore, the energy levels of the GO and TMD layers can be modulated by chemical doping and simple surface treatment. Therefore, it is assumed that the GO and TMD layers can be used as the HELs in the PSCs instead of PEDOT:PSS.

Here, we demonstrate that GO, MoS_2, and WS_2 can be used as the HELs in the PSCs instead of PEDOT:PSS. The GO layer was synthesized through the Hummers' method and the TMD layers such as MoS_2 and WS_2 layers were obtained by the chemical vapor deposition (CVD) method. It is shown that the perovskite structure was well-formed on the GO and TMD layers. Therefore, the performance of the PSCs based on the GO and TMD layers was comparable with that of the PEDOT:PSS-based ones. From these results, the working principle of the GO and TMD layers as the HELs in the PSCs is investigated.

2. Experimental details

2.1. Synthesis of MoS_2 and WS_2

The insulating substrate, SiO_2 (300 nm)/Si wafer, was prepared using a standard piranha solution and conventional cleaning procedures based on acetone, isopropyl alcohol, and de-ionized (DI) water bath sonication. Two precursor solutions were prepared with a 5 mM concentration of each $(NH_4)_2MoS_4$ and $(NH_4)_2WS_4$ in ethylene glycol. For the optimized precursor coating conditions, the cleaned substrates were subjected to the O_2 plasma and the UV-O_3 surface treatment for 15 min. The substrates were spin-coated with the precursor solution at 3500 rpm for 60 s. A thermal CVD system involving high purity hydrogen (H_2) and nitrogen (N_2) gas was used for the thermolysis of the precursor films. First, the temperature of the CVD furnace was set to 500 °C for 30 min, under H_2 and N_2 gas flow at 1 Torr pressure. The H_2 and N_2 flow rates were controlled by the mass flow controllers at a rate of 40 cm^3/min for H_2 and 200 cm^3/min for N_2. Then, the thermolysis was gradually initiated under the H_2 gas at a relatively high temperature. After the pre-heating step, the temperature was significantly increased to approximately 950 °C. When the CVD furnace temperature reached 950 °C, the samples were placed on the heating zone for 1 h, and another heating zone with sulfur powder was turned on to initiate sulfur sublimation. After 60 min of thermolysis, the furnace was cooled to room temperature at a rate of 10–15 °C/min under 40 sccm and 200 sccm of H_2 and N_2 flow, respectively. A schematic illustration of MoS_2 and WS_2 synthesis is shown in Fig. 1(a). Poly [methyl methacrylate] (PMMA) was then spin-coated on the synthesized MoS_2 and WS_2 layers. Then, the substrate was immersed into a hydrogen fluoride and aluminum fluoride (1:1) bath at room temperature for 1 h to etch away the SiO_2 layers. Subsequently, the remaining MoS_2 and WS_2 layers were carefully dipped into a DI water bath 7–9 times to remove any residual etchant. The MoS_2 and WS_2 sheets were then transferred onto an indium tin oxide (ITO) substrate. Finally, the PMMA membrane was removed by an acetone bath at 50 °C for 30 min after which the PMMA/MoS_2 (or WS_2) layer had completely adhered to the target substrate.

2.2. Synthesis of graphene oxide (GO)

GO was synthesized by the oxidation of natural graphite powder according to the Hummers' method with $NaNO_3$. Briefly, 1 g natural graphite powder (universal grade, 200 mesh, 99.9995%; Alfa Aesar) and 1 g $NaNO_3$ were stirred in 46 mL concentrated H_2SO_4 for 4 h in an ice bath. After stirring, 6 g $KMnO_4$ was added gradually, taking care not to increase the temperature of the solution more than 20 °C. After $KMnO_4$ and the solution were mixed, the suspension was heated at 35 °C and stirred for 2 h. Next, 92 mL of DI water was added, and the solution was stirred for 15 min at 98 °C. By adding 200 mL of DI water and 14 mL H_2O_2 (30%) slowly, the color of the solution changed from black to orange. The solution was separated through centrifugation at 8000 rpm and removed except for the GO precipitation. This GO precipitation was washed with 900 mL of 1:8 HCl aqueous solution. The centrifugation at 8000 rpm for 10 min and the washing steps were repeated at least three times to remove any metal ions. After that, the cleaning using only the DI water was repeated about seven times. Finally, the GO was dried at 50 °C for 12 h in a vacuum oven. The schematic illustration of the GO synthesis is shown in Fig. 1(b).

2.3. Synthesis of perovskite precursor

Hydroiodic acid (10 mL, 57 wt% in water, Aldrich) and methyl-amine (22 mL, 33% in ethanol, Aldrich) were stirred in the ice bath for 3 h. Next, the solution was evaporated at 90 °C using a rotary evaporator to remove the ethanol and DI water. Then, the dissolution of the precipitate into anhydrous ethanol and recrystallization with diethyl ether were performed three times forming methylammonium iodide (CH_3NH_3I). To prepare a perovskite