



## Letter

## Layered bismuth selenide utilized as hole transporting layer for highly stable organic photovoltaics

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## ABSTRACT

Layered bismuth selenide (L-Bi<sub>2</sub>Se<sub>3</sub>) nanoplates were implemented as hole transporting layers (HTLs) for inverted organic solar cells. Device based on L-Bi<sub>2</sub>Se<sub>3</sub> showed increasing power conversion efficiency (PCE) during ambient condition storage process. A PCE of 4.37% was finally obtained after 5 days storage, which outperformed the ones with evaporated-MoO<sub>3</sub> using poly(3-hexylthiophene) (P3HT) as donor material and [6,6]-phenyl-C61-butyric acid methyl ester (PC<sub>61</sub>BM) as acceptor. The improved device efficiency can be attributed to the high conductivity and increasing work function of L-Bi<sub>2</sub>Se<sub>3</sub>. The work function of L-Bi<sub>2</sub>Se<sub>3</sub> increased with the storage time in ambient condition due to the oxygen atom doping. Ultraviolet photoelectron spectroscopy and high resolution X-ray photoelectron spectroscopy were conducted to verify the increased work function, which originated from the p-type doping process. The device based on L-Bi<sub>2</sub>Se<sub>3</sub> exhibited excellent stability in ambient condition up to 4 months, which was much improved compared to the device based on traditional HTLs.

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## 1. Introduction

Organic solar cells have drawn increasing research attention due to its light weight, low fabrication cost and the potential of large area commercial production [1,2]. With the great achievements in synthesis of donor polymers, which aim to obtain novel polymers with narrow band gap and low highest occupied molecular orbital (HOMO), the power conversion efficiency (PCE) of organic solar cells have achieved more than 10% for single junction geometry in recent years [3–6]. Apart from the innovation in active layer materials, interfacial layer materials also play key roles in organic photovoltaics because of their selective transporting properties toward different charge carriers and Ohmic contact at the interfaces [7]. Typical cathode interfacial layer materials mainly contain titanium oxide [8], zinc oxide [9–12], cesium carbonate [13] and [(9,9-bis(3-(N,N-dimethylamino)propyl)-2,7-fluorene)-alt-2,7-(9,9-dioctylfluorene)] [14,15]. The work function (WF) of these materials are all close to the lowest unoccupied molecular orbitals (LUMO) level of [6,6]-phenyl-C61-butyric acid methyl ester (PC<sub>61</sub>BM), which facilitates the extraction of electrons from the active layer. On the other hand, poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) [16], molybdenum

trioxide (MoO<sub>3</sub>) [17], nickel oxide [18] and tungsten trioxide [19] are typical anode interfacial materials, which help to transport holes or block leaking electrons. However, due to the acidic property and hygroscopic nature of PEDOT:PSS, replacement with inorganic material has drawn wide interests in order to prolong the life time of devices [20]. Although devices based on transition metal oxide show much improved stability than the ones based on PEDOT:PSS, the expense on fabrication facilities and energy cost are not ideal for future development. In addition, solution processed metal oxides usually requires high temperature annealing process to enhance their electronic properties, and even though the defects could not be avoided [21,22].

Recently, layered two-dimensional materials (2D-materials) attract tremendous attentions due to large surface area, high carrier mobility and less defect states lay on the surface [23–28]. In previous reports, we have reported solution processed layer molybdenum sulfide (MoS<sub>2</sub>) and niobium selenide (NbSe) nanoplates that utilized as efficient anode buffer layer in organic solar cells. An improved performance compared with evaporated-MoO<sub>3</sub> (e-MoO<sub>3</sub>) based devices was obtained [29,30]. We ascribed the improved efficiencies mainly to the proper energy levels and less-trapped anode buffer layer film, where the traps states were mainly located at the edge of nanoplates.

Bismuth selenide (Bi<sub>2</sub>Se<sub>3</sub>) is a typical topological insulators material, which shows high surface conductivity. However, it acts

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as insulator in its bulk form [31,32]. Here, layered-Bi<sub>2</sub>Se<sub>3</sub> (L-Bi<sub>2</sub>Se<sub>3</sub>) was used as hole transporting layer (HTL). Freshly fabricated devices based on L-Bi<sub>2</sub>Se<sub>3</sub> only showed moderate PCE. However, after 5 days ambient storage process, device based on poly(3-hexylthiophene) (P3HT) and PC<sub>61</sub>BM composite materials achieved a PCE of 4.37%. Compared with conventional transition metal oxide charge transport materials, L-Bi<sub>2</sub>Se<sub>3</sub> shows higher conductivity and crystallization, and can be easily solution processed at room temperature. Besides that, an impressive device stability of 4 months in ambient condition is observed. According to ultraviolet photoelectron spectroscopy (UPS) results, WF of L-Bi<sub>2</sub>Se<sub>3</sub> increased with being stored in ambient condition. This phenomenon was lined well with the increasing of device efficiencies, especially the growing values of open circuit voltage ( $V_{oc}$ ). X-ray photoelectron spectroscopy (XPS) measurements were also conducted to investigate the changes of oxygen elements during the air exposure process.

## 2. Experimental

### 2.1. Materials

O-dichlorobenzene (ODCB) (Sigma Aldrich 99.9%), 2-isopropanol (IPA) (Alfa Aesar, 99.9%), zinc acetate hydrate (Zn(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O, Alfa Aesar, 98.0%) and 2-methoxy ethanol (CH<sub>3</sub>OCH<sub>2</sub>CH<sub>2</sub>OH, Alfa Aesar, 99.0%) were used as received without further purification. P3HT and PC<sub>61</sub>BM were purchased from 1-Material Co. Ltd. The patterned ITO substrates were purchased from Shenzheng South Glass Ltd. with a resistance of 10 Ω/□.

### 2.2. Solution preparation

L-Bi<sub>2</sub>Se<sub>3</sub> was obtained through the reaction of lithium intercalation. 80 mg Bi<sub>2</sub>Se<sub>3</sub> solid powder was mixed with 10 mL *n*-butyl lithium and stirred at room temperature for ~48 h. The composites were then washed with extra hexane for three times to get rid of any organic residues and impurities. 40 mL distilled water was added into the precipitate prior to putting into sonication bath for ~1 h. And after removing the precipitate under low rotation centrifuging, the mixed composites were washed with distilled water for several times. The suspension of L-Bi<sub>2</sub>Se<sub>3</sub> was dispersed into IPA with a concentration ~0.3 mg/mL. The Bi<sub>2</sub>Se<sub>3</sub> nanoplates concentration was estimated by weighting the precipitate after evaporating the solvent. The 2D grazing incidence X-ray diffraction (2D-GIXD) of the Bi<sub>2</sub>Se<sub>3</sub> nanoplates layer was conducted at BL14B station of the Shanghai Synchrotron Radiation Facility (SSRF).

ZnO was prepared according to previous report [33]. And typically, 1.00 g zinc acetate dihydrate was dissolved in the mixture of 2-methoxyethanol (10.0 mL) and ethanolamine (275 μL) under stirred overnight in ambient environment. The precursor solution was stored into refrigerator at 10 °C after filtered through 0.45 μm filter.

### 2.3. Device fabrication

All the devices were fabricated based on an inverted structure (ITO/ZnO/P3HT:PC<sub>61</sub>BM/L-Bi<sub>2</sub>Se<sub>3</sub>/Ag). The reference devices with e-MoO<sub>3</sub> as HTLs were also fabricated. The ITO substrates were cleaned with IPA, acetone, ethanol and deionized water for sequence and then treated with UV-ozone for 15 min before usage. ZnO precursor solution was spin-coated on top of ITO with a rotation speed of 4000 r.p.m and annealed at 150 °C in ambient condition. Then P3HT:PC<sub>61</sub>BM blend solution was spin-coated at 700 r.p.m for 18 s. The wet substrates were stored into petro dish until totally dry (~30 min). The substrates were then annealed at

110 °C for 12 min in glovebox. After the substrates were cooled down to room temperature naturally, the fresh prepared L-Bi<sub>2</sub>Se<sub>3</sub> solution was spin-coated multi-times on top of active layer at 4000 r.p.m to obtain films with different coverage ratio. The devices were finished with 80-nm-thick silver electrode with a base pressure of  $2 \times 10^{-6}$  mTorr (Kurt J. Lesker Ltd.). The active area of each pixel was patterned with a shadow mask with area of ~7.25 mm<sup>2</sup> for each one.

### 2.4. Device characterizations

Current–voltage ( $J$ – $V$ ) curves of devices under illumination were tested under a simulated irradiation at 100 mW/cm<sup>2</sup>. And light intensity was calibrated by a Newport standard silicon solar cell 91150. EQE spectra were measured by Newport monochromator 74125 and power meter 1918. All the electrical statistics of  $J$ – $V$  and external quantum efficiency (EQE) curves were obtained through a Keithley 2612. Atomic force microscopy (AFM) images are all taken by a MultiMode V (Veeco) in tapping mode. WF of Bi<sub>2</sub>Se<sub>3</sub> is obtained by UPS spectra. Chemical composition was determined by XPS measurement (KRATOS AXIS Ultra DLD).

## 3. Results and discussions

The L-Bi<sub>2</sub>Se<sub>3</sub> nanoplates were prepared by the lithium chemical intercalation. Lithium ions penetrated into the space between bismuth and selenide in organic solvent due to its small size. Then these inserted lithium ions can generate hydrogen bubbles upon water addition. Finally, the relatively large thin L-Bi<sub>2</sub>Se<sub>3</sub> plate can be obtained in aqueous solution. Zeta potential value of aqueous exfoliated Bi<sub>2</sub>Se<sub>3</sub> was over ~50 mV, which indicated the surface potential could offer the large surface charge to avoid the nanoplates agglomeration [34]. Ultraviolet–visible (UV–Vis) absorption spectrum of Bi<sub>2</sub>Se<sub>3</sub> nanoplates suspended in water was depicted in Fig. 1a. The absorption peak appeared at ~550 nm. The absorption spectrum displayed smooth curve in the whole range, which indicating a high-quality suspension with little light scattering [35]. Transmission electron microscope (TEM) images of exfoliated L-Bi<sub>2</sub>Se<sub>3</sub> were depicted in Fig. 1b and c. According to the TEM images, a large proportion of the L-Bi<sub>2</sub>Se<sub>3</sub> was layered structure with high specific surface area. The inserted picture in Fig. 1b was the fast Fourier transforms (FFT) image, indicating monolayer property of the prepared Bi<sub>2</sub>Se<sub>3</sub>. The image in Fig. 1c and the inserted one displayed a very smooth surface of L-Bi<sub>2</sub>Se<sub>3</sub>. Synchrotron-radiation-based grazing incidence X-ray diffraction (GIXD) spectrum of exfoliated L-Bi<sub>2</sub>Se<sub>3</sub> was depicted in Fig. 1d. The image depicted in Fig. S1 was the corresponding semi-ring pattern of the 2D-GIXD of the L-Bi<sub>2</sub>Se<sub>3</sub> nanoplates. According to the spectrum, L-Bi<sub>2</sub>Se<sub>3</sub> were oriented with (003) and (006)-axis in plane, which verified that L-Bi<sub>2</sub>Se<sub>3</sub> preferentially faced on top of active layer.

The device structure (ITO/ZnO/P3HT:PC<sub>61</sub>BM/L-Bi<sub>2</sub>Se<sub>3</sub>/Ag) was depicted in Fig. 2a. P3HT:PC<sub>61</sub>BM blend was spin-coated as active layer and L-Bi<sub>2</sub>Se<sub>3</sub> acted as HTL. Here in order to optimize device performance, devices based on L-Bi<sub>2</sub>Se<sub>3</sub> were fabricated by multi-times spin-coating process of L-Bi<sub>2</sub>Se<sub>3</sub> suspension. All the devices were tested and stored in ambient condition without any encapsulation. It was found that the performance of our devices increased with storage time, which was very different from the standard devices based on e-MoO<sub>3</sub>. The output statistics of devices based on L-Bi<sub>2</sub>Se<sub>3</sub> with twice spin-coating process were used as an example. In the initial stage, typically 4–5 days, the open circuit voltage ( $V_{oc}$ ), the short-circuit current ( $J_{sc}$ ), the fill factor (FF) and the PCE of the device increased steadily.  $J$ – $V$  curves of the device stored in air for different time were depicted in Fig. 2b. All the

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