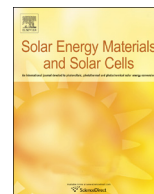




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## Solution-processable bismuth iodide nanosheets as hole transport layers for organic solar cells

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## ABSTRACT

In this paper we demonstrate the use of low-temperature-solution-processable bismuth iodide ( $\text{BiI}_3$ ) nanosheets as hole transport layers in organic photovoltaics with an active layer comprising poly(3-hexylthiophene) (P3HT) mixed with a fullerene derivative. The performance of the resulting devices was comparable with that of corresponding conventionally used systems incorporating polyethylenedioxythiophene:polystyrenesulfonate (PEDOT:PSS). UV–vis spectroscopy revealed that the transparency of a  $\text{BiI}_3$  layer in the visible ( $> 620$  nm) and near-infrared range is greater than that of a PEDOT:PSS layer. X-ray photoemission spectroscopy of a  $\text{BiI}_3$  film revealed signals at 158.8, 164, 618.6, and 630 eV—characteristic of  $\text{Bi } 4f_{7/2}$ ,  $\text{Bi } 4f_{5/2}$ ,  $\text{I } 3d_{5/2}$ , and  $\text{I } 3d_{3/2}$ , respectively—that indicated a stoichiometric  $\text{BiI}_3$  film. Wet milling of  $\text{BiI}_3$  crystals resulted in the formation of nanosheets, the presence of which we confirmed using scanning electron microscopy. The resultant power conversion efficiency of the device was approximately 3.5%, with an open-circuit voltage of 0.56 V, a short-circuit current density of  $10.4 \text{ mA cm}^{-2}$ , and a fill factor of 60.1% under AM1.5G irradiation ( $100 \text{ mW cm}^{-2}$ ).

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## 1. Introduction

Harnessing natural energy might be the best approach toward satisfying today's growing world energy demands, with solar energy the undisputed frontrunner among all such sources. Organic photovoltaics (OPVs) based on polymeric materials are promising candidates for harvesting solar energy for various reasons, including simple solution-processability, light weight [1], mechanical flexibility and transparency [2,3], and the ability to produce solar panels on large scale at low cost [4–6]. In particular, solution-processed bulk heterojunction (BHJ) solar cells are receiving much attention because of their superior mechanical robustness, easy blending, and high power conversion efficiencies (PCEs). Devices incorporating blends of regioregular poly(3-hexylthiophene) (P3HT) as the electron donor and phenyl  $\text{C}_{61}$ -butyric

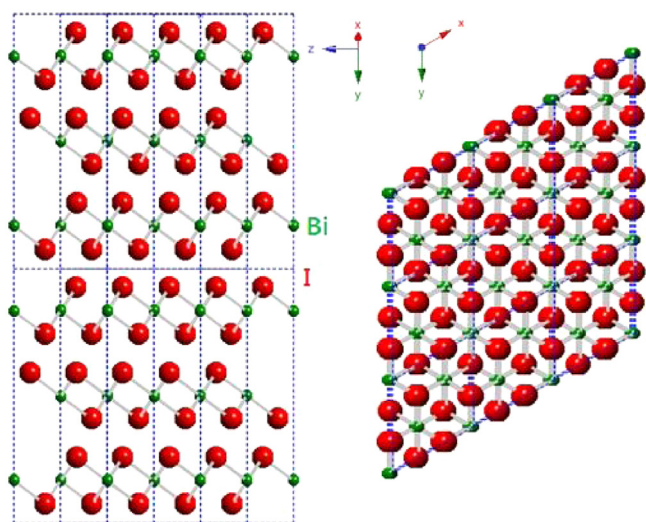
acid methyl ester (PCBM), a soluble fullerene derivative, as the acceptor have reached PCEs of 3–5% [7,8]. P3HT forms long, thin conducting nanowires and PCBM forms more-homogeneous nanocrystalline films when annealed. The importance of annealing during processing cannot be overestimated; it increases phase separation, crystallization, and the photophysical and transport properties of the active layer [7].

A buffer layer is an important constituent between the electrode and active layer; it plays the crucial role of extracting and transporting the photogenerated carriers (holes or electrons). While it allows movement of one kind of the carrier, it blocks the passage of the other through an energy mismatch, often resulting in a dramatic increase in PCE [9–11]. Polyethylenedioxythiophene:polystyrenesulfonate (PEDOT:PSS) is used widely as a standard anode buffer layer as well as standalone indium tin oxide (ITO)-free anode in OPVs because of its excellent transporting properties, high transparency, and smooth textured surface [12–15]. Nevertheless, because of its acidic and hygroscopic nature, PEDOT:PSS can interact physically and chemically with adjoining layers, thereby degrading device performance [16,17]. In the quest for replacements for

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**Fig. 1.** Crystal structure of  $\text{BiI}_3$ ; the Bi and I atoms are displayed as green and red spheres, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

PEDOT:PSS, researchers have identified various metal oxide hole transport materials such as tungsten oxide ( $\text{WO}_3$ ) [18–20], molybdenum oxide ( $\text{MoO}_3$ ) [20–22], nickel oxide ( $\text{NiO}_x$ ) [23], and vanadium oxide ( $\text{V}_2\text{O}_5$ ) [20,24] for OPVs with improved device performance. However, these materials require stringent conditions of high vacuum, high temperature processing and high power consumption which increases the resulting cost of fabrication. Solution processable alternatives like graphene oxide (GO) [25,26] are attracting interest due to their various advantages.

Herewith we show synthesis of solution processable  $\text{BiI}_3$  nanosheets and effectively demonstrated as hole transport layer (HTL) for OPVs.  $\text{BiI}_3$  is a layered semiconducting material having a wide band gap (ca. 2 eV) [27–30]; it has potential applications in room-temperature  $\gamma$ -ray detectors [31] and X-ray digital imaging sensors [32]. Recently, appreciable interest has been shown in the optical properties of  $\text{BiI}_3$  because of its strong intrinsic optical anisotropy [27,33,34].  $\text{BiI}_3$  adopts a layered structure (Fig. 1) with  $\text{Bi}^{3+}$  ions establishing six-fold coordination with  $\text{I}^-$  ions, which adopt non-linear two-fold coordination with I–Bi–I angles close to  $90^\circ$ . The Bi–I bonds are highly ionic with the 6p electrons of the Bi atoms transferred to the I atoms. The I–Bi–I layers are held together through weak van der Waals forces, allowing  $\text{BiI}_3$  crystals to be cleaved readily along the [001] direction; such weak van der Waals bonding does, however, make this material soft and difficult to handle.

## 2. Experimental

### 2.1. Chemicals

Sodium tellurite (99%), bismuth(III) nitrate pentahydrate (99.99%), iodine (99.99%), polyvinylpyrrolidone (PVP; MW=40,000), ethylene glycol (EG, 99%), hydrazine monohydrate (64–65%), acetic acid (99.7%), isopropanol (99.5%), ethanol (99.99%), and acetone (99.9%) were purchased from Sigma–Aldrich and used without further purification.

### 2.2. Synthesis of $\text{BiI}_3$ crystals

A solution of  $\text{NaTeO}_3$  (0.3 M) in EG (5 mL), a solution of  $\text{Bi}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (0.3 M) in EG (3.5 mL), PVP (0.5 g), acetic acid (3 mL), and hydrazine monohydrate (0.5 mL) were added to EG (50 mL) and stirred for 20 min. The resulting homogeneous solution

was transferred to a 100-mL Teflon-lined stainless-steel autoclave. The sealed vessel was then heated at  $160^\circ\text{C}$  for 2 h then cooling to room temperature. Acetone (20 mL) was added and then the product was separated through centrifugation (12,000 rpm, 1 h) and washed several times with a mixture of acetone and ethanol. The final product was dried in an oven at  $80^\circ\text{C}$  overnight. A solution of  $\text{Bi}_2\text{Te}_3$  (0.1 M) in water (25 mL) and a solution of  $\text{I}_2$  (0.6 M) in water (25 mL) were mixed and then stirred for 30 min; the resulting homogeneous solution was transferred to a 100-mL Teflon-lined stainless-steel autoclave. The sealed vessel was then heated at  $180^\circ\text{C}$  for 10 h before cooling to room temperature. Deionized water (100 mL) was added and then the product separated through centrifugation (12,000 rpm, 1 h) and washed several times with a mixture of water and ethanol (75:25 mL). The final product was dried in an oven at  $80^\circ\text{C}$  overnight.

The synthesis was based on the disproportionation of  $\text{I}_2$ :



Elementary step



In the hydrothermal process, the pH of the reaction system decreased to less than 1. Thus, it is believed that single crystals of  $\text{BiI}_3$  were soluble in hot water under strong acidic conditions. In addition, the instability of HIO [see Eq. (3)] meant that the reaction did not produce  $\text{BiOI}$ , consistent with the X-ray diffraction (XRD) data. The influence of the reaction time and temperature on the preparation of crystalline  $\text{BiI}_3$  was also investigated; the optimal conditions for the formation of highly crystalline  $\text{BiI}_3$  were a temperature of  $180$ – $190^\circ\text{C}$  for 10–15 h. If the reaction temperature was below  $170^\circ\text{C}$  or the reaction time was less than 6 h, the yield of  $\text{BiI}_3$  diminished and the as-synthesized  $\text{BiI}_3$  was poorly crystalline.

### 2.3. $\text{BiI}_3$ nanosheets: preparation and characterization

The resultant  $\text{BiI}_3$  crystals were dispersed in isopropanol (0.25 wt%) and ground to a fine powder at room temperature using a homemade grinder operated at 2000 rpm for 120 min [35]. The solvent and weight-percentage of  $\text{BiI}_3$  crystals were optimized based on device performance (see Figs. S1 and S2 and Tables S1 and S2 in Supplementary information). No surfactant or modifying agents were added during grinding. The resultant suspension containing  $\text{BiI}_3$  nanosheets was kept for a long period to check its stability; no further precipitation was observed. Powder XRD patterns were recorded at room temperature—using a Bruker D8 X-ray diffractometer equipped with a diffracted beam monochromator set for Cu  $\text{K}\alpha$  radiation ( $\lambda=1.54056\text{ \AA}$ )—in the  $2\theta$  range  $10$ – $80^\circ$  with a step size of  $0.01655^\circ$  and step time of 0.4 s. Transmission spectra of the films were measured using a Jacobs V-670 UV–Vis spectrophotometer. Scanning electron microscopy (SEM) images were recorded using an FEI Noval 200 scanning electron microscope (15 kV). X-ray photoelectron spectroscopy (XPS) was performed using a PHI 5000 Versa Probe equipped with an Al  $\text{K}\alpha$  X-ray source (1486.6 eV). Atomic force microscopy (AFM) images of spin-coated  $\text{BiI}_3$  films were recorded using a Veeco di Innova instrument operated in the tapping mode.

### 2.4. Device fabrication and characterization

ITO-Coated glass substrates ( $<10\ \Omega\ \text{sq}^{-1}$ , RiTdisplay) were cleaned through ultrasonication—once in detergent (20 min) and subsequently twice in deionized (DI) water (20 min each)—and then dried under  $\text{N}_2$  gas and before placing in an oven overnight.

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