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Thin-film formation of 2D MoS_2 and its application as a hole-transport layer in planar perovskite solar cells

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ABSTRACT

We have introduced centrifugally-cast thin-film formation technique to 2D transition metal dichalcogenides (TMDs) formed through a liquid based exfoliation method. The film-formation technique has evidenced a growth of uniform and homogeneous thin-films of single or a-few-layered MoS_2; the thin-films have been introduced as a charge-transport layer in perovskite solar cells. From scanning tunneling spectroscopy and thereof the density of states of the 2D semiconductor, we have observed that the band-edges of MoS_2 formed a type-II band-alignment with the commonly-used organic-inorganic lead halide ($CH_3NH_3PbI_3$) perovskite when the 2D material was subjected to an ozone-treatment. We thereafter formed *p–i–n* heterojunction planar perovskite solar cells with the thin-film of 2H-MoS_2 so that charge separation can occur at the MoS_2|perovskite interface. In this work, we also report device characteristics and impedance spectroscopy of the heterojunctions, which were optimized for a small series-resistance and a large shunt-resistance.

1. Introduction

Inorganic compounds with a layered-structure, such as transition metal dichalcogenides (TMDs), have recently attracted considerable attention due to their unique physical properties [1]. Unlike semi-metallic graphene, TMDs with a 2H crystal arrangement have band gaps suitable for many opto-electronic applications [2]. Layer number dependent band gap and indirect to direct band gap crossover during multilayer to monolayer/bilayer transition have made this class of materials rich in chemical physics [3–5]. Amongst the layered TMDs, MoS_2 is one of the most widely-studied semiconductor; accordingly, many researchers have introduced MoS_2 as a channel material for high performance unipolar or ambipolar field-effect transistors (FETs) [6–8]. Intrinsic band gap, chemical inertness of the basal-plane flake surface [7], extraordinary sunlight absorption capability or a high extinction coefficient coupled with a high value of carrier mobility [9] indicate the promise of layered MoS_2 in solar cell technologies. The potential of MoS_2 has been reflected in a few interesting attempts to evidence photovoltaic properties [10,11]. Apart from its role as an absorber layer, a high carrier-mobility and a relatively large band gap of MoS_2 are indicative of its potential as a charge-transport material in solar cells [12–14].

So far as the synthesis of single-layered to a few-layered TMD sheets is concerned, both bottom-up approaches like chemical vapor deposition (CVD) and top-down approaches, such as electrochemical [15] and mechanical or sonication-assisted exfoliation processes have been employed effectively [16]. In contrast to the success of single-layered TMD nanosheet formation, the method to form thin-films of the layered material is yet to reach the desired grade. For successful application of these single-layered TMDs in solar cells, it is of prime importance to form their large-area and uniform thin-films at a moderate cost. Among the typically employed procedures, films grown through CVD method in general provide uniform surface coverage over a large-area at the expense of high-fabrication cost. Other common solution-based approaches, namely spin- and drop-cast methods and spray-coating technique are indeed cost-effective [13,14,17]. However, they are expected to leave serious defects in the form of restacking and aggregation [17] in addition to pin-holes in as-grown films due to a little dispersibility of the flakes. Use of such films in device architectures has hence remained below the acceptance level. Due to these constraints, application of layered TMDs as the active material for opto-electronic devices is yet to take off. Their use as charge-transport materials could however be envisaged [12–14,18].

Among the non-traditional approaches, Sivula and his group proposed an impressive strategy to use surface ligand modified TMD sheets in order to increase dispersivity and hence to fabricate pin-hole free films; space-charge-limited conduction process was studied through these films [17]. The ligands, namely alkyl-trichlorosilane, however remained in the thin-film and thereby affected carrier conduction process. Sivula and his group also introduced space-confined self-

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assembly approach through the use of a liquid/liquid interface formed between two non-solvents for the TMD flakes; the approach enabled strong confinement and superior self-assembly of WSe_2 for photoelectrochemical hydrogen production [19]. However presence of surface ligands and comparatively complex film-formation procedure remained as major roadblocks for the use of these films in photovoltaic applications.

In this work, in order to form large-area and uniform thin-films of single and a-few-layered MoS_2 sheets, we have introduced the method of centrifugal-casting. This low-cost film-formation procedure has earlier been used for ceramics and metals and is being used in large-scale industrial applications [20]. In recent years, Sergeant and his group have utilized this method to form thin-films of PbS nanoparticles in fabricating high-efficiency solar cells [21].

For 2D materials, this film-deposition technique will have added advantages. Since the centrifugal-casting occurs according to weight of the nanosheets, we expected that the large-area flakes would more likely be deposited as compared to the smaller ones. This is based on the consideration that a prolonged exfoliation process followed by centrifugation did not leave thicker TMDs in the solution.

In order to verify the functional effectiveness of centrifugally-cast films of single or a-few-layered MoS_2, we introduced such films as a transport-layer in methylammonium lead triiodide ($CH_3NH_3PbI_3$ or $MAPbI_3$) based perovskite solar cells. It may be recalled that a tremendous potential of the hybrid perovskites have been revealed of late [22]. At its early stage, perovskite solar cells were an exact mimic of dye-sensitized solar cells (DSSCs), where the hybrid perovskite played the role of a sensitizer like N719 dye [23]. A paradigm shift occurred with the discovery that the perovskite itself can separate charge carriers and also play the role of electron- and hole-transport layers due to their ambipolar nature. Considering widespread success of the perovskite, it has become the star material in the world of solar cells, although stability of the cells remained a topic of intense research [24–26].

We therefore aimed to introduce MoS_2 thin-films formed through the centrifugally-cast technique to perovskite solar cells. The $MoS_2|CH_3NH_3PbI_3$ combination, if found to be energetically suitable, would allow us to form *p–i–n* structures without the use of Spiro-OMeTAD at the light-entering side. Despite the phenomenal success of Spiro-OMeTAD as a hole-transport layer in perovskite photovoltaics [27], its cost, atmospheric stability, promotion to interfacial iodine migration, and so forth have necessitated its replacement [28].

In this direction, single-layered MoS_2 sheets, exfoliated from van der Waals bonded bulk crystals are uncharged, chemically inert, and highly stable in ambient conditions. In this work, we therefore aimed to introduce centrifugally-cast thin-films of a few-layered MoS_2 in perovskite solar cells. Apart from establishing successful film-formation of MoS_2, we have demonstrated solar cell applications in *p–i–n* heterojunctions arising out of efficient hole-transfer from $MAPbI_3$ to MoS_2.

2. Experimental

2.1. Materials

While MoS_2 powder was purchased from Sigma-Aldrich Chemical Company, methylammonium iodide (CH_3NH_3I) was purchased from Dyenamo AB, Sweden. Phenyl-C61-butyric acid methyl ester (PCBM) (99%) was purchased from M/s SES Research, Houston, TX.

2.2. Exfoliation of MoS_2

To obtain a large quantity of a few-layered MoS_2, liquid-based exfoliation method was followed [29]. To do so, 0.5 g of MoS_2 powder was added to 10 mL N-methyl-2-pyrrolidone (NMP) that acted as the exfoliating agent. The mixed solution, kept in a beaker, was sonicated for 4–5 h while maintaining a temperature of 5 °C to avoid overheating. During the sonication, the black solution tuned dark-green indicating the success of the exfoliation process. There was also a remarkable change in dispersibility of the solution. To obtain ample amount of exfoliated TMDs while maintaining a reasonable sheet dimension, the sonication process was continued for 20 h in steps. The solution was allowed to settle overnight resulting in a dark-green solution with some bulk MoS_2 powder as a precipitate. The upper portion contained a-few-layered MoS_2 sheets which were separated by centrifugation at 3000 rpm for 30 min. To collect specifically the a-few-layered sheets, the top three-fourth of the supernatant was collected. The resultant solution had a MoS_2 concentration of approximately 1 mg/mL. The material was characterized through optical absorption spectroscopy, X-ray diffraction (XRD) analysis, and transmission electron microscopy (TEM) and high-resolution TEM (HR-TEM) images. The measurements were carried out with a Shimadzu UV–2550 spectrophotometer, Bruker D8 Advanced X–ray powder diffractometer (Cu K_α radiation, λ = 1.54 Å), and Jeol JEM-2100F TEM, respectively.

2.3. Formation of centrifugally-cast thin-films of 2D MoS_2 nanosheets

In order to execute the centrifugal-casting film-formation method, MoS_2 in 0.2 mL of NMP was first added to 40 mL of ethanol in a 50 mL centrifuge tube. A substrate was immersed at the bottom of the tube at a particular angle, so that deposition due to centrifugal force would occur on the desired surface. The tube with the substrate was centrifuged at 8000 rpm, which amounted to a relative centrifugal force of 7168*g*, for 10 min. Additional MoS_2 solution (0.2 mL) was added without removing the content along with the substrate from the tube so that the centrifugal casting method can be repeated in cycles to obtain a desired thickness of MoS_2 thin-films. Finally, the substrate was removed from the centrifuge tube and kept in a vacuum desiccator for removal of residual solvent. Since the repeated centrifugation process was carried out in ethanol, a thermal annealing was not mandatory; here ethanol easily evaporated within 10 min under vacuum. The thin-films were characterized through optical absorption spectroscopy, scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, and atomic force microscopy (AFM). The measurements were carried out with a JEOL JSM 6700F field emission SEM, a XPS instrument (Omicron: Serial no. 0571), a Horiba Jobin-Yvon Raman triple grating spectrometer system (model number T64000) using 514.5 nm excitation of an Argon-ion laser source (Stabilite 2017, Spectra Physics), and a Nanosurf Easyscan2 Atomic Force Microscope (AFM) in a non-contact mode. In addition, the TMDs were characterized through scanning tunneling spectroscopy (STS) using a Nanosurf Easyscan2 scanning tunneling microscope (STM) in an ambient condition. To do so, ultrathin films of the material were deposited on highly-doped silicon wafers (*n*-type, 3–10 mΩ cm) by the same centrifugal casting method. From tunneling current through a monolayer, we determined differential tunnel conductance (dI/dV) that has correspondence to density of states (DOS) of the semiconductor. This enabled us to locate conduction and valence band-edges (CB and VB, respectively) of the exfoliated TMD nanosheets with respective to their Fermi energy. Since bias was applied to the tip with respect to the substrate, the tip at a positive voltage withdrew electrons from the semiconductor; peaks in the positive voltage of DOS spectra therefore inferred location of its VB. Similarly, peaks at negative tip-voltages, at which electrons could be injected to the semiconductor, provided location of the CB edge.

2.4. Formation of perovskite thin-films and fabrication of solar cells

Perovskite solar cells having a sandwiched geometry were fabricated on indium tin oxide (ITO) coated glass substrates. The TMD film acted as a hole-transport layer (HTL). The HTL coated ITO substrates were subjected to a short oxygen plasma treatment for 30 s. Immediately thereafter, the treated MoS_2-coated ITO substrates were transferred into a glove-box for the formation of a perovskite layer.

A two-step sequential spin-coating method was adopted to form