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2D black phosphorous nanosheets as a hole transporting material in perovskite solar cells

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Abstract:

We demonstrate for the first time liquid exfoliated few layers of 2D Black phosphorus (BP) nanosheets as a hole transporting material (HTM) for perovskite based solar cells. The photoelectron spectroscopy in air (PESA) measurements confirms the low lying valence band level of BP nanosheets (-5.2 eV) favourable for hole injection from $\text{CH}_3\text{NH}_3\text{PbI}_3$ (MAPbI₃). We have recorded ~25% improvement in power conversion efficiency (PCE) of $\eta=16.4\%$ for BP nanosheets + Spiro-OMeTAD as an HTM as compared to spiro-OMeTAD ($\eta=13.1\%$). In addition, we report the PCE of $\eta=7.88\%$ for the device structure of FTO/BL TiO₂/Meso TiO₂/MAPbI₃/BP nanosheets/Au where exfoliated BP nanosheets are acting as HTM without any further additives. While PCE, $\eta=4\%$ was recorded for devices fabricated without HTM (FTO/BLTiO₂/MesoTiO₂/MAPbI₃/Au). Photoluminescence (PL) quenching of MAPbI₃ and impedance measurements further confirm the charge extraction ability of BP nanosheets. The structural and optical characterization of liquid exfoliated BP nanosheets is discussed in detail with the aid of transmission electron microscopy, Raman spectroscopy, absorption spectroscopy and photo-electron spectroscopy.

Introduction:

Organic–inorganic metal halide perovskite based solar cells, (with the general formula of ABX_3 , where A is an organic cation, B is commonly Pb^{2+} , and X is a halide) have attracted extensive attention of photovoltaic researchers due to their immense progress in device performance from 3.8% to 22.1% [1-4]. Hybrid organic-inorganic perovskite materials have excellent photovoltaic properties such as high absorption coefficient, tunable band gaps and long electron–hole diffusion lengths [1, 5-10].

Typically, in a perovskite solar cell, the perovskite absorbing layer is sandwiched between an electron transporting material (ETM) and a hole transporting material (HTM). The ETMs are either compact metal oxides (e.g TiO_2 / ZnO / SnO_2 etc) or organic materials (fullerene (C_{60}) and phenyl- C_{61} -butyric acid methyl ester (PCBM)) while HTMs are organic, inorganic or polymeric materials [3, 11-14]. Spiro-OMeTAD (2,2',7,7'-Tetrakis-(N,N-di-p-methoxyphenylamine)-9, 9'-spirobifluorene) and PTAA (Poly (triarylamine)) are the two commonly used HTMs in perovskite solar cells[15, 16] and have played a crucial role in achieving high cell performance. However, the high costs, thermal and chemical instability of these materials hinder the viable commercialization of perovskite solar cells. Hence there is a need for alternative HTMs with low cost while still maintaining high efficiency. The key criteria for the selection of HTMs in perovskite solar cell is that the energy level of the valence band maximum (highest occupied molecular orbital (HOMO)) of HTM should be lower than that of the perovskite with suitable hole mobility and good thermal stability[17].

Recently, a number of two-dimensional (2D) materials including transition metal dichalcogenides (TMDs) have been proposed as potential candidates in electronics and optoelectronics due to their excellent tunable opto-electronic properties and their high carrier mobility with ambipolar characteristics[18-25]. However, these 2D semiconducting materials are prepared either by micromechanical exfoliation (which has ultra-low yield) or CVD approach which is a laborious and expensive technique. Further, reduced graphene oxide and graphene oxide are employed as hole conductor in perovskite solar cells and organic solar cells [25-28]. However, the graphene oxide possesses intrinsic disadvantages for HTMs such as an insulating nature and a high degree of oxygen content.

Black phosphorous (called as phosphorene in monolayer) is emerging as a promising 2D nanomaterial due to its suitable electronic and optoelectronic properties [29]. It is a van der Waals-bonded layered material with carrier mobility up to $\sim 1000 \text{ cm}^2/\text{V.s}$ at room temperature (RT) [30, 31]. BP exhibits layer dependent direct band gap ranging from $\sim 0.3 \text{ eV}$

(bulk) to ~2 eV (monolayer) and has received remarkable attention since its direct band gap nature is independent of layer number. Recently, the viability of phosphorene as a buffer layer for perovskite based solar cells has also been demonstrated [32, 33]. The high optical transparency, good charge carrier mobility and extraordinary electronic properties at low costs open the possibility of it being employed as an HTM. However, the use of BP as an HTM has not been explored yet.

Here, we have validated liquid exfoliated few layers of 2D BP (BP nanosheets) as a potential buffer as well HTM layer for perovskite based solar cells. These BP nanosheets are further characterized by electron microscopy, Raman spectroscopy, absorption spectroscopy and photo-electron spectroscopy to confirm its structure and energy levels. Surprisingly, the improved power conversion efficiency (PCE) of $\eta=16.4\%$ have been achieved for perovskite based solar cells employing BP nanosheets + Spiro-OMeTAD as an HTM as compared to spiro-OMeTAD ($\eta=13.1\%$). Furthermore, thin films of BP nanosheets are incorporated as a hole transporting material (HTM) in multi-layered perovskite solar cell. The power conversion efficiency (PCE), $\eta=7.8\%$ is achieved ($J_{sc}=17.0\text{ mA/cm}^2$, $V_{oc} 0.84\text{ V}$ and $FF=54.7\%$) using BP nanosheets as an HTM. The effect of BP nanosheets on perovskite layer is corroborated by effective PL quenching at the perovskite-BP interface indicating efficient charge transfer. Furthermore, Electrochemical Impedance spectroscopy (EIS) measurements were also carried out at different applied bias to understand the charge transport properties of HTM. Our results indicate that solvent processed inorganic BP nanosheets as a potential HTM that can replace the conventional organic HTMs in perovskite based solar cells.

Results and discussion:

Liquid phase exfoliation (LPE) process was employed to exfoliate few layers of black phosphorus (BP) nanosheets from bulk BP crystals (as purchased) in anhydrous NMP solvent using probe sonication method [34]. LPE is appropriate for the large-scale production of black phosphorus and proven for other 2D nanomaterials also [35]. The size and the concentration of exfoliated BP nanosheets in NMP were controlled by tuning the exfoliation and centrifugation isolation procedures. The morphology and characterizations of as exfoliated BP nanosheets are shown in figure 1. Field emission scanning electron microscopy image (Figure 1a) confirms that BP nanosheets are randomly orientated with dense packing (Figure 1a). High magnification image of BP nanosheet (Figure 1b) indicates the atomically thin nature of BP nanosheet on holey carbon grid.

Figure-1 Characterization of the as-exfoliated BP nanosheets. (a) FE-SEM image of BP nanosheets, inset of figure (a) is the digital image of exfoliated BP nanosheets in NMP solvent, (b) FE-SEM image (TED mode) of single BP nanosheet on holey carbon grids, (c) size distribution histogram of BP nanosheets, (d, e) HRTEM images of BP nanosheets, inset of (d) is the selected area electron diffraction (SAED) pattern, and (f) Raman spectroscopy of as exfoliated BP nanosheets.

The lateral size distribution histogram of exfoliated BP nanosheets is shown in figure 1c, which reveals the average length of BP nanosheets (~ 100 nanosheets measured) is $\langle L \rangle = 1114 \pm 63$ nm. The HRTEM image of the BP nanosheets (Figure 1d & 1e) shows the lattice spacing of ~ 0.3 nm which corresponds to that of the (021) crystal planes [36, 37]. The corresponding SAED pattern consists of discrete spots indicating the high crystallinity of exfoliated BP nanosheets (inset in Figure 1d). Raman spectroscopy was performed on drop casted BP nanosheets to confirm the characteristic peaks of the exfoliated sample. A typical Raman spectrum of few layered BP nanosheets reveals signatures of one out-of-plane A_g^1 (356 cm^{-1}) and two in-plane B_{2g} (429 cm^{-1}) and A_g^2 (457 cm^{-1}) phonon vibrational modes which are in good accordance with previous observations for BP[38] (figure 1f). To further clarify the valence states of exfoliated BP nanosheets, we acquired X-ray photoelectron spectroscopy (XPS) data with monochromatic Al K α radiation ($h\nu = 1486.7 \text{ eV}$). The wide-scan survey spectrum (shown in Figure S1a) only shows the presence of O 1s, C 1s, and doublet P 2p signals. Figure S1b shows the high resolution XPS of BP nanosheets, where

2p_{3/2} and 2p_{1/2} doublet at 129.5 and 130.3 eV, respectively, characteristic of elemental phosphorus[34]. Small oxidized phosphorus (i.e., P_xO_y) sub-bands at higher energy region around 133.8 eV is observed, an indication of the minor oxidation of BP nanosheets which is a fundamental stability issue with BP [34].

Thus, exfoliated and characterized BP nanosheets are used as HTM in perovskite based solar cells. Subsequently, in order to find the valence band position of exfoliated BP nanosheets, photoelectron spectroscopy in air (PESA) measurements have been carried out by preparing uniform thin film of BP nanosheets at optimized concentrations (BP/IPA suspension~6 mg/ml) on ITO substrate. The cross over point is identified as ionization potential or valence band maximum obtained from PESA measurement which is 5.2 eV (Figure 2a). This indicates that, valence band position of the BP nanosheets is at lower energy level than the perovskite valence band (-5.4 eV), which provides the driving force for hole injection from the perovskite layer to BP nanosheets (figure 2b). The valence band energy level of BP nanosheets (-5.2 eV) is fairly matching with commonly used organic hole-transporting material spiro-OMeTAD[15] in perovskite based devices. The conduction band energy level (-3.4 eV) was calculated by addition of band gap value (1.8 eV) to the valence band level (-5.2 eV). The band gap of BP (1.8 eV) was calculated from UV-Vis absorption measurements of BP nanosheets by using Tauc plot as shown below figure S2. After assessing the energy levels of BP nanosheets, we have fabricated solar cell devices using conventional architecture as depicted in figure 2d. The details of device fabrication are provided in experimental section. Concisely, the device structure consists of FTO/BL TiO₂/mesoporous TiO₂/MAPbI₃/BP nanosheet film/Au. Blocking layer of TiO₂ layer was deposited by spray pyrolysis method on FTO glass, followed by mesoporous TiO₂ layer (~300 nm). Then, MAPbI₃ was deposited using single step deposition method. The BP nanosheets dispersed in isopropyl alcohol (IPA) with appropriate concentration (~6 mg/ml in anhydrous IPA solvent) was spin coated on perovskite layer followed by the Au electrode evaporation (~110 nm). The concentration of the BP nanosheet in IPA is optimised based on the preliminary experiments in order to achieve the maximum surface coverage on the perovskite in order to minimise shunting at the perovskite-Au interface. The obtained device data is compared with that of the most commonly used organic HTM i.e spiro-OMeTAD. Figure 2c exhibits the characteristic current density (J_{sc}) vs voltage (V) curve of the best performing perovskite based device using BP nanosheets as HTM. The obtained power conversion efficiency (PCE)

is 7.88% with open circuit potential (V_{OC}) of 0.84 V, current density (J_{SC}) of 17.0 mA/cm², and fill factor (FF) of 0.54 under one sun illumination (AM1.5 100 mW/cm²).

Figure-2 (a) Photo-electron spectroscopy in air (PESA) measurement data shows the ionization potential of BP nanosheets is 5.2 eV, (b) Band alignment of perovskite solar cells with BP nanosheets as HTM, (c) J-V curve of perovskite solar cells with BP nanosheets as HTM (blue colour) and without HTM (black colour), (d) schematic diagram of perovskite solar cells with BP nanosheets as HTM, (e) FE-SEM image of BP nanosheets on MAPbI₃, and (f) cross-sectional FE-SEM image of the fabricated perovskite solar cell with BP nanosheets as HTM.

The reference devices were also fabricated under similar experimental conditions using the conventional spiro-OMeTAD as an HTM with device architecture consists of: i) FTO/BLTiO₂/mesoporousTiO₂/MAPbI₃/spiro-OMeTAD/Au), ii) without HTM i.e.FTO/BL TiO₂/mesoporous TiO₂/ MAPbI₃/Au and iii) using BP nanosheets in combination with spiro-OMeTAD i.e. (FTO/BL TiO₂/mesoporous TiO₂/ MAPbI₃/BP nanosheets/spiro-OMeTAD Au.

Table-1 *J-V characteristic values of perovskite solar cell with BP nanosheets as HTM and without HTM*

HTM Samples	J _{sc} (mA/cm ²)	V _{oc} (V)	FF (%)	η (%)
BP nanosheets	17.09	0.84	54.7	7.88
Without HTM	14.0	0.59	48.4	4.0

The achieved device performance based on above mentioned device architectures are tabulated in Table 1 and Figure S3, S4. The device efficiency achieved with BP nanosheets as HTM (η=7.88%) is higher to that of the device fabricated without HTM (η=4.0%), which is mainly due to the improvement in J_{sc} (22%), V_{oc} (42%) and FF (13%). In general, parasitic resistances, series (R_s) and shunt (R_{sh}) mainly affect the FF factor of the solar cell and hence the efficiency. The contribution for the R_s is mostly from the resistance of all components that comes in the path of current and hence higher the R_s value lower the current. On the other hand, the R_{sh} is due to the leakage at P-N junction, hence lower the R_{sh} higher the V_{oc}. The R_s values for device fabricated with and without BP HTM are 79.8 Ω and 32.4 Ω as well R_{sh} are 4462.2 Ω and 1008.6 Ω respectively. The higher value of R_s in case of BP HTM suggests that resistance contribution from the thicker BP layer (~2μm) as compared to that of without HTM under similar device fabrication condition. Surprisingly, higher value of R_{sh} in case of BP HTM suggested the low leakage path way and reduced recombination and hence better J_{sc}, V_{oc} and FF and hence efficiency (η) as compared to that of without HTM. This suggests the hole selectivity of BP nanosheets, which reduces the interfacial recombination, enhancing the device performance in comparison with the device fabricated without HTM.

Figure-3 (a) Power conversion efficiency (PCE) of 14 perovskite solar devices (BP nanosheets as HTM), and (b) Photoluminescence quenching of MAPbI₃ perovskite with BP nanosheets

Device performance of the BP nanosheets as HTM is lower in assessment with conventional spiro-OMeTAD as HTM which is mainly due to the decrement in Voc (20% decrease) and FF (24% decrease). This perhaps due to the poor surface coverage of the BP nanosheets on the top of the perovskite layer as shown in figure 2e, which may reduce pathways for charge transfer to BP as well as allows for increased recombination. Besides, the BP overlayer thickness is $\sim 2 \mu\text{m}$ and it is rough in nature, which adversely affects the thermal deposition of top Au electrode. It suppresses an effective charge transfer (BP/Au interface), increases charge recombination, reduces Voc and hence the device performance. Also, the decrease in Rsh and increase in Rs have been noticed for the BP-HTM devices in comparison with that of Spiro-HTM. The overlayer thickness ($\sim 2 \mu\text{m}$) of the BP nanosheets is much larger than that of spiro-OMeTAD thickness ($\sim 150 \text{ nm}$, Figure S5). Indeed, the ability for spiro-OMeTAD to be doped as well as low thicknesses of the organic HTM are advantages. As substrate surface coverage is one of the challenges and limitations of 2D materials [39], and experiments are in progress to improvise the surface coverage and reduce the BP layer thickness. In order to check reproducibility, the perovskite based devices were fabricated under similar experimental conditions using BP nanosheets as HTM. The average (out of 14 devices) power conversion efficiency obtained for BP nanosheets as HTM devices is $\eta = 6.80 \pm 0.8\%$ (Figure 3a). Interestingly, device fabricated using combination of BP+spiro-OMeTAD as

HTM ($\eta=16.4\%$) (Figure S6) showed better performance than standalone spiro-OMeTAD only ($\eta=13.1\%$) and BP nanosheets ($\sim 7.88\%$). The improvement in performance is mainly due the boost in J_{sc} (17%) and FF (4.5%). As mentioned earlier, that BP overlayer thickness is $\sim 2\text{ }\mu\text{m}$, rough in nature as well there is no coverage. It is likely that the spiro-OMeTAD may infiltrate beneath the uncovered portion of BP and forms direct contact with MAPbI_3 , which further improves the charge collection. The decrement of R_s and increment in R_{sh} for BP+ Spiro as an HTM as compared to BP HTM has been noted. Incident photon to current conversion efficiency (IPCE) of the fabricated solar cell devices with different architectures are shown in figure S7. The low IPCE in the range of 500 to 800 nm, for the BP nanosheets based HTM points to inefficient charge collection between the perovskite layer and BP nanosheets [40]. Photoluminescence (PL) quenching was performed to further confirm the charge extraction ability of BP nanosheets as hole-conducting material in contact with the perovskite absorber. The films for PL quenching measurements are prepared as per standard procedures as described in experimental section. Accordingly, the perovskite film was spin coated on the glass substrate and subsequently BP nanosheets were deposited on top of the perovskite layer. Similarly, the reference sample was also prepared with pristine perovskite and perovskite/Spiro-OMeTAD on glass substrate. The pristine perovskite was excited at 550 nm and observed emission at 770 nm. This is in good agreement with the reported values [41]. The suppression in the PL intensity of perovskite peak was noted for BP nanosheets as well as Spiro-OMeTAD covered perovskite samples as shown in figure 3b and figure S8. The pronounced PL quenching of perovskite charge carriers after BP coating was clear signature of the effective charge transfer from perovskite to BP (50% PL quenching). We noted that PL quenching by BP can be further enhanced by improving nanosheets coverage.

Figure-4: (a) Equivalent circuit modal used for fitting electrochemical impedance spectroscopic (EIS) EIS data, R_s –sheet resistance, R_{rec} -recombination resistance and CPE_{chem} -chemical capacitance at TiO_2 /perovskite (interface1), R_{HTM} -resistance, CPE_{HTM} -capacitance at perovskite/BP (interface 2), (b) representative superimposed Nyquist plot of solar cell device fabricated using BP HTM at 0 mV, 225mV and 450 mV dc applied bias, (c) hole transport resistance (R_{HTM}) with respect applied bias for BP and Spiro at different applied bias, (d) electrical conductivity of the BP and Spiro. EIS measurements were carried at frequency range 1 MHz to 10 Hz, different applied bias 100 mV to 1000 mV, voltage perturbation of 10 mV amplitude for BP HTM and Spiro HTM, Dot represents the experimental data and solid line indicate the fitted data

Electrochemical Impedance spectroscopy (EIS) measurements of the devices fabricated using BP nanosheets and Spiro-OMeTAD as HTMs were performed to investigate the interfacial charge transport properties. Accordingly, the EIS measurements were carried out at frequency ranges from 1 MHz to 10 Hz at different applied biases with a perturbation of 10 mV amplitude (Autolab 302 N). The spectra were fitted using Z-View software (figure 4a).

Figure 4b exhibits the representative superimposed Nyquist plots of cell fabricated using BP nanosheets as an HTM at 0 mV, 225 mV and 450 mV applied dc bias. The two arcs are observed *viz* at high and low frequency region commonly ascribed to the charge transfer process occurring at counter electrode i.e. perovskite/HTM interface and TiO_2 /perovskite interface respectively. The arc in the Nyquist plots becomes smaller with respect to applied bias, because of the increase in the charge carrier concentration at the interface, and this is the common phenomenon noticed in mesoscopic devices[42-44]. Figure 4c illustrates the hole transport resistance (R_{HTM}) extracted from high frequency region of devices with BP and Spiro-OMeTAD HTMs with respect to different applied dc bias. The hole conductivity in each cell generally increases with respect to applied bias voltage due to the higher hole density in HTL as a consequence of hole injection from perovskite to HTM. The charge transfer resistance is higher in case of BP HTM as compared to Spiro-OMeTAD implies lower FF of the BP HTM devices as compared to Spiro-OMeTAD. The results are in agreement with that of obtained J-V data. In addition, the superimposed Nyquist plot of perovskite devices based on the BP nanosheets, Spiro-OMeTAD and mixed BP nanosheets + Spiro-OMeTAD as an HTM is shown in figure S9. The EIS measurement clearly indicate that the overall charge transfer resistance of the perovskite device fabricated using the BP nanosheets as HTM is higher than that of Spiro as an HTM, which is mainly attributed to the thicker BP nanosheets layer ($\sim 2 \mu\text{m}$). Also, the surface roughness of the BP layer adversely affecting on the thermal deposition of top Au electrode as well as suppressing the effective charge transfer (BP/Au interface) (as discussed in the preceding part of the manuscript). Surprisingly, overall resistance of the device fabricated with mixed HTM is observed to be decreased (the diameter of the arc is reduced), mainly because of the Spiro-OMeTAD infiltration through BP layer, which further improves charge transfer process at perovskite/HTM interface.

However, the conductivity of the BP HTM is greater than that of Spiro-OMeTAD (Figure 4d). Here σ_{HTM} was estimated from R_{HTM} as $\sigma_{\text{HTM}} = L / (R_{\text{HTM}} A)$ where L is the length calculated as HTM overlayer thickness as measured by SEM. In general, the higher hole conductivity leads to a lower voltage loss and higher fill factor. The lower FF for BP-HTM based devices as compared to Spiro-OMeTAD is mainly attributed to poor contact of the BP nanosheets with perovskite due to incomplete coverage. In addition as mentioned earlier, along with the poor surface coverage of the BP nanosheets, larger overlayer thickness ($\sim 2 \mu\text{m}$) along with rough surface, adversely effects on the BP/Au interface. It suppresses an

effective charge transfer, increases charge recombination, reduces V_{oc} and hence the device performance. The experiments are in progress to improvise the interfacial contact for better device performance.

Figure-5: Aging of perovskite solar cells with BP nanosheets and Spiro-OMeTAD as hole transporting material: Power conversion efficiency (η), short circuit current density (J_{sc}), open circuit voltage (V_{oc}) and fill factor over 528 hours (432 hr under inert atmosphere and 96 hrs under 65% humidity) without encapsulation.

Stability is a major issue in perovskite solar cells, and degradation of perovskite as well as spiro-OMeTAD occurs upon exposure to moisture, oxygen, UV radiation and temperature. Accordingly, preliminary device stability of the BP nanosheets as well as spiro-OMeTAD HTM based perovskite devices without as encapsulation was monitored for few weeks in an

inert as well as humid condition (65%) as illustrated in Figure 5. The devices are quite stable over weeks in an inert atmosphere (stored inside argon filled glove box), however 60% of degradation in their initial performance was noticed after storing the devices in 65% humidity which might be an intrinsic material problem that need to be focussed in future to improve the BP stability under humid environment.

Conclusions

In conclusion, liquid exfoliated BP nanosheets are successfully applied as a HTM in perovskite based solar cell devices for the first time. We have achieved ~25% improvement in power conversion efficiency (PCE) of $\eta=16.4\%$ for BP nanosheets + Spiro-OMeTAD as an HTM as compared to spiro-OMeTAD ($\eta=13.1\%$). In addition, the power conversion efficiency of ~7.8% is achieved with device architecture of FTO/blocking layer TiO_2 /mesoporous TiO_2 / MAPbI_3 /BP/Au where MAPbI_3 act as absorbing layer and BP act as hole conducting material. The charge transport mechanism was proved by using PL and impedance measurements. The results are promising and indicate that solvent processed black phosphorus can be a potential HTM for the use in optoelectronics devices such as solar cells, LEDs and photo-detectors.

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References

- [1] A. Kojima, K. Teshima, Y. Shirai, T. Miyasaka, Journal of the American Chemical Society, 131 (2009) 6050-6051.
- [2] M.M. Lee, J. Teuscher, T. Miyasaka, T.N. Murakami, H.J. Snaith, Science, 338 (2012) 643-647.

- [3] M. Saliba, T. Matsui, J.-Y. Seo, K. Domanski, J.-P. Correa-Baena, M.K. Nazeeruddin, S.M. Zakeeruddin, W. Tress, A. Abate, A. Hagfeldt, M. Grätzel, *Energy & Environmental Science*, 9 (2016) 1989-1997.
- [4] N.J. Jeon, J.H. Noh, Y.C. Kim, W.S. Yang, S. Ryu, S.I. Seok, *Nat Mater*, 13 (2014) 897-903.
- [5] Q. Dong, Y. Fang, Y. Shao, P. Mulligan, J. Qiu, L. Cao, J. Huang, *Science*, 347 (2015) 967-970.
- [6] T.J. Savenije, C.S. Ponseca, L. Kunneman, M. Abdellah, K. Zheng, Y. Tian, Q. Zhu, S.E. Canton, I.G. Scherblykin, T. Pullerits, A. Yartsev, V. Sundström, *The Journal of Physical Chemistry Letters*, 5 (2014) 2189-2194.
- [7] G. Xing, N. Mathews, S. Sun, S.S. Lim, Y.M. Lam, M. Grätzel, S. Mhaisalkar, T.C. Sum, *Science*, 342 (2013) 344-347.
- [8] G. Xing, N. Mathews, S.S. Lim, N. Yantara, X. Liu, D. Sabba, M. Grätzel, S. Mhaisalkar, T.C. Sum, *Nat Mater*, 13 (2014) 476-480.
- [9] S.A. Kulkarni, T. Baikie, P.P. Boix, N. Yantara, N. Mathews, S. Mhaisalkar, *Journal of Materials Chemistry A*, 2 (2014) 9221-9225.
- [10] D.P. Nenon, J.A. Christians, L.M. Wheeler, J.L. Blackburn, E.M. Sanehira, B. Dou, M.L. Olsen, K. Zhu, J.J. Berry, J.M. Luther, *Energy & Environmental Science*, 9 (2016) 2072-2082.
- [11] J.-Y. Jeng, Y.-F. Chiang, M.-H. Lee, S.-R. Peng, T.-F. Guo, P. Chen, T.-C. Wen, *Advanced Materials*, 25 (2013) 3727-3732.
- [12] H.J. Snaith, A. Abate, J.M. Ball, G.E. Eperon, T. Leijtens, N.K. Noel, S.D. Stranks, J.T.-W. Wang, K. Wojciechowski, W. Zhang, *The Journal of Physical Chemistry Letters*, 5 (2014) 1511-1515.
- [13] P. Docampo, J.M. Ball, M. Darwich, G.E. Eperon, H.J. Snaith, *Nature Communications*, 4 (2013) 2761.
- [14] Z. Li, S.A. Kulkarni, P.P. Boix, E. Shi, A. Cao, K. Fu, S.K. Batabyal, J. Zhang, Q. Xiong, L.H. Wong, N. Mathews, S.G. Mhaisalkar, *ACS Nano*, 8 (2014) 6797-6804.
- [15] D. Bi, W. Tress, M.I. Dar, P. Gao, J. Luo, C. Renevier, K. Schenk, A. Abate, F. Giordano, J.-P. Correa Baena, J.-D. Decoppet, S.M. Zakeeruddin, M.K. Nazeeruddin, M. Grätzel, A. Hagfeldt, *Science Advances*, 2 (2016).
- [16] W.S. Yang, J.H. Noh, N.J. Jeon, Y.C. Kim, S. Ryu, J. Seo, S.I. Seok, *Science*, 348 (2015) 1234-1237.
- [17] P. Dhingra, P. Singh, P.J.S. Rana, A. Garg, P. Kar, *Energy Technology*, 4 (2016) 891-938.
- [18] Q.H. Wang, K. Kalantar-Zadeh, A. Kis, J.N. Coleman, M.S. Strano, *Nat Nano*, 7 (2012) 699-712.
- [19] T. Roy, M. Tosun, J.S. Kang, A.B. Sachid, S.B. Desai, M. Hettick, C.C. Hu, A. Javey, *ACS Nano*, 8 (2014) 6259-6264.
- [20] M.-L. Tsai, S.-H. Su, J.-K. Chang, D.-S. Tsai, C.-H. Chen, C.-I. Wu, L.-J. Li, L.-J. Chen, J.-H. He, *ACS Nano*, 8 (2014) 8317-8322.
- [21] M. Bernardi, M. Palummo, J.C. Grossman, *Nano Letters*, 13 (2013) 3664-3670.
- [22] X. Li, S. Lin, X. Lin, Z. Xu, P. Wang, S. Zhang, H. Zhong, W. Xu, Z. Wu, W. Fang, *Opt. Express*, 24 (2016) 134-145.
- [23] X. Gu, W. Cui, T. Song, C. Liu, X. Shi, S. Wang, B. Sun, *ChemSusChem*, 7 (2014) 416-420.
- [24] X. Gu, W. Cui, H. Li, Z. Wu, Z. Zeng, S.-T. Lee, H. Zhang, B. Sun, *Advanced Energy Materials*, 3 (2013) 1262-1268.
- [25] J.-M. Yun, J.-S. Yeo, J. Kim, H.-G. Jeong, D.-Y. Kim, Y.-J. Noh, S.-S. Kim, B.-C. Ku, S.-I. Na, *Advanced Materials*, 23 (2011) 4923-4928.

- [26] A. Priyadarshi, L.J. Haur, P. Murray, D. Fu, S. Kulkarni, G. Xing, T.C. Sum, N. Mathews, S.G. Mhaisalkar, *Energy & Environmental Science*, (2016).
- [27] Z. Wu, S. Bai, J. Xiang, Z. Yuan, Y. Yang, W. Cui, X. Gao, Z. Liu, Y. Jin, B. Sun, *Nanoscale*, 6 (2014) 10505-10510.
- [28] J.-S. Yeo, R. Kang, S. Lee, Y.-J. Jeon, N. Myoung, C.-L. Lee, D.-Y. Kim, J.-M. Yun, Y.-H. Seo, S.-S. Kim, S.-I. Na, *Nano Energy*, 12 (2015) 96-104.
- [29] V. Eswaraiah, Q. Zeng, Y. Long, Z. Liu, *Small*, 12 (2016) 3480-3502.
- [30] L. Li, Y. Yu, G.J. Ye, Q. Ge, X. Ou, H. Wu, D. Feng, X.H. Chen, Y. Zhang, *Nat Nano*, 9 (2014) 372-377.
- [31] H. Liu, A.T. Neal, Z. Zhu, Z. Luo, X. Xu, D. Tománek, P.D. Ye, *ACS Nano*, 8 (2014) 4033-4041.
- [32] M. Batmunkh, M. Bat-Erdene, J.G. Shapter, *Advanced Materials*, 28 (2016) 8586-8617.
- [33] S. Lin, S. Liu, Z. Yang, Y. Li, T.W. Ng, Z. Xu, Q. Bao, J. Hao, C.-S. Lee, C. Surya, F. Yan, S.P. Lau, *Advanced Functional Materials*, 26 (2016) 864-871.
- [34] D. Hanlon, C. Backes, E. Doherty, C.S. Cucinotta, N.C. Berner, C. Boland, K. Lee, A. Harvey, P. Lynch, Z. Gholamvand, S. Zhang, K. Wang, G. Moynihan, A. Pokle, Q.M. Ramasse, N. McEvoy, W.J. Blau, J. Wang, G. Abellan, F. Hauke, A. Hirsch, S. Sanvito, D.D. O'Regan, G.S. Duesberg, V. Nicolosi, J.N. Coleman, *Nature Communications*, 6 (2015) 8563.
- [35] K.R. Paton, E. Varrla, C. Backes, R.J. Smith, U. Khan, A. O'Neill, C. Boland, M. Lotya, O.M. Istrate, P. King, T. Higgins, S. Barwich, P. May, P. Puczkarski, I. Ahmed, M. Moebius, H. Pettersson, E. Long, J. Coelho, S.E. O'Brien, E.K. McGuire, B.M. Sanchez, G.S. Duesberg, N. McEvoy, T.J. Pennycook, C. Downing, A. Crossley, V. Nicolosi, J.N. Coleman, *Nat Mater*, 13 (2014) 624-630.
- [36] Z. Sun, H. Xie, S. Tang, X.-F. Yu, Z. Guo, J. Shao, H. Zhang, H. Huang, H. Wang, P.K. Chu, *Angewandte Chemie International Edition*, 54 (2015) 11526-11530.
- [37] P. Yasaei, B. Kumar, T. Foroozan, C. Wang, M. Asadi, D. Tuschel, J.E. Indacochea, R.F. Klie, A. Salehi-Khojin, *Advanced Materials*, 27 (2015) 1887-1892.
- [38] R. Fei, L. Yang, *Applied Physics Letters*, 105 (2014) 083120.
- [39] A. Capasso, F. Matteocci, L. Najafi, M. Prato, J. Buha, L. Cinà, V. Pellegrini, A.D. Carlo, F. Bonaccorso, *Advanced Energy Materials*, 6 (2016) 1600920-n/a.
- [40] S. Ma, H. Zhang, N. Zhao, Y. Cheng, M. Wang, Y. Shen, G. Tu, *Journal of Materials Chemistry A*, 3 (2015) 12139-12144.
- [41] A.S. Subbiah, A. Halder, S. Ghosh, N. Mahuli, G. Hodes, S.K. Sarkar, *The Journal of Physical Chemistry Letters*, 5 (2014) 1748-1753.
- [42] Y. Yang, J. Xiao, H. Wei, L. Zhu, D. Li, Y. Luo, H. Wu, Q. Meng, *RSC Advances*, 4 (2014) 52825-52830.
- [43] P.P. Boix, G. Larramona, A. Jacob, B. Delatouche, I. Mora-Seró, J. Bisquert, *The Journal of Physical Chemistry C*, 116 (2012) 1579-1587.
- [44] V. Gonzalez-Pedro, E.J. Juarez-Perez, W.-S. Arsyad, E.M. Barea, F. Fabregat-Santiago, I. Mora-Sero, J. Bisquert, *Nano Letters*, 14 (2014) 888-893.