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ARTICLE TYPE

Chemical origin of the p-type and n-type doping effects in the hybrid methylammonium - lead iodide (MAPbI₃) perovskite solar cells

Lyubov A. Frolova, Nadezhda N. Dremova and Pavel A. Troshin*

In the present Communication we discuss a field-induced and photoinduced self-doping chemistry resulting in the formation of the positively and negatively charged vacancies in the MAPbI₃ perovskite films. These vacancies induce p-
10 **type and n-type doping of the perovskite absorber leading to the realization of the p-i-n device operation mechanism.**

The hybrid solar cells based on the complex methylammonium or formamidium lead iodides (MAPbI₃ or FAPbI₃, respectively) have shown recently efficiencies
15 exceeding 20%.[1-2] At the same time, thin films and crystals of MAPbI₃ and FAPbI₃ demonstrated rather outstanding electronic properties such as exciton binding energy as low as 2 meV, [3] electron-hole diffusion lengths exceeding 150 μm and charge carrier mobility >100 cm²V⁻¹s⁻¹.[4] Perovskite
20 crystals show very low density of trap states (~10^{10} per cm³) comparable to the characteristics of the best-quality crystalline silicon.[5] The internal quantum efficiencies of the optimized perovskite solar cells approach 100% in a wide spectral region thus revealing the efficient charge generation
25 and negligible charge recombination in these devices.[3]

The aforementioned fantastic electronic characteristics of the perovskite semiconductors fall in a strong contradiction with the "dirty" chemistry which is typically used for their preparation. It is rather remarkable that the solar cell
30 performances do not suffer much from the presence of an excessive amount of organic iodide (MAI or FAI) in the films. Moreover, introducing various inorganic (e.g. HI or NH₄Cl) or organic (1,8-diiodooctane or N-cyclohexyl-2-pyrrolidone) additives or partial replacing MA with larger cations can even
35 improve the photovoltaic performance of the material.[6] These examples prove unprecedented tolerance of the hybrid perovskite absorbers to the presence of chemical impurities in the structure of their films which makes a sharp contrast to conventional inorganic (e.g. silicon) and organic (e.g.
40 fullerene-polymer) photovoltaics.[7] This is a reason why many researchers are seeking for alternative explanations for the highly efficient operation of the perovskite solar cells.[8]

It has been proposed recently that perovskite solar cells represent p-i-n devices where p-type doping is induced by the
45 presence of lead and methyl ammonium vacancies (V_{Pb} and V_{MA}), while n-doping results from the presence of iodide vacancies (V_I) as it follows from the theoretical calculations.[9] It is believed that doping can be achieved in MAPbI₃ by using different MAI and PbI₂ ratios in the precursor solutions.[9-1]
50 Xiao et. al. have reported recently that drift of ions in the perovskite films might induce the p- and n- doping of th layers adjacent to the corresponding electrodes resulting in the p-i-n device structure.[11] A particular important finding was bleaching of the MAPbI₃ perovskite films in the regio
55 adjacent to one of the electrodes in the lateral diode-type device under the applied electrical field.[11] Surprisingly, authors of this report did not comment on the chemical natur of the observed bleaching effect.

In the present work we attempted to reveal the chemistry
60 occurring in the perovskite films under the applied electri field. The top-electrode and bottom-electrode lateral device with the distance between the electrodes of 70-90 μm fille with MAPbI₃ active material were fabricated (Fig. 1a-b). Th current-voltage characteristics in dark and under differen
65 illumination conditions revealed no significant difference between the bottom-contact and top-contact devices with except for somewhat higher currents delivered by the former It is notable that we did not observe any photovoltaic effect i these lateral structures before performing any polarizatio
70 experiments (see below). However, a strong photoconductivity was revealed in these systems in line with a recent report of Gottesman et. al.[12] For example, the curr flowing under the 37 mW/cm² monocromatic green light (λ=532 nm) illumination conditions at the bias of 80 V is 500-
75 2000 times higher as compared to the dark current value (Fig 1c-f).

We reproduced the polarization experiment described by Xiao et.[11] by applying a potential of 100 V to our lateral devices in dark for 2 hrs. Examination of the perovskite films with th
80 optical microscopy just after the polarization revealed rathe interesting results. First of all, there was a noticeabl bleaching of the material adjacent to one of the electrode suggesting the formation of PbI₂. At the same time, multipl dark-colored islands appeared in the area nearby the counter
85 electrode. Moreover, the perovskite film between two electrodes showed strong gradients in color. In particulary, the central part of the film was considerably darker a compared to the regions disposed closer to the electrodes o the device (Fig. 2a). Notably, this kind of color distributio
90 disappears in ca. 20-30 min. after the polarization experiment suggesting that the system evolves towards a quasiequilibriu state *via* diffusion and redistribution of some chemical
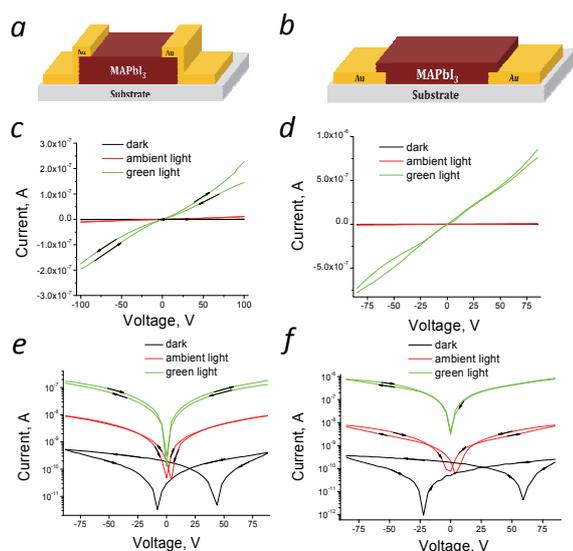
species.

Figure 1. A schematic layout of the top contact (a) and bottom contact (b) lateral devices with MAPbI3 films. Current-voltage characteristics of the top contact (c, e) and bottom contact (d, f) devices in linear (c, d) and logarithmic (e, f) scales under the ambient light (0.35 mW/cm^2) and monochromatic green light (37 mW/cm^2) before performing any polarization experiments.

The degradation of the MAPbI$_3$ films under the applied electric field was also confirmed by the contact-mode AFM measurements performed for the top contact devices. Indeed, the polarization resulted in the formation of cavities in the areas adjacent to both electrodes (Figs. 2b-c). One can notice also different morphology of the materials adjacent to the cathode and to the anode.

The chemical composition of the perovskite films was probed using energy-dispersive X-ray spectroscopy (EDXS) analysis. We note that all samples prior to the measurements were pumped down to a high vacuum (ca. 10^{-8} mbar) in a work chamber of a Zeiss LEO Supra scanning electron microscope (GEMINI). The time of vacuuming was sufficiently long (2-6 h), so we were able to examine only a quasiequilibrium composition of the material in the device channel with no chance to probe the initial state induced by polarization which is shown on the optical microphotograph in Fig. 2a. Nevertheless, the EDXS analysis allowed us to reveal noticeable gradients in the composition of the perovskite films while going from one electrode to another. Fig. 2d shows that the area adjacent to anode is considerably enriched in iodine. The iodine-to-lead (I : Pb) atomic ratio well exceeds the value of 3.0 which is characteristic for the normal MAPbI$_3$ films. The extra iodine could be trapped in the form of triiodide (I_3^-) or $[PbI_6]^{4-}$ ions known from the literature.[13] The I : Pb ratio gradually decreases while moving away from the anode and then sharply drops down to 2.3±0.2 in the area adjacent to cathode. This observation implies the formation of PbI$_2$ as one of the cathode products of the perovskite decomposition. It should be noted that the perovskite film covered by the edges of the gold electrodes has a noticeably different composition in comparison with the neighboring regions in the channel of the lateral device.

Probing the nitrogen-to-lead (N : Pb) ratio was not that illustrative. Nitrogen is a very light atom, therefore instrumental error in its determination was quite high. Nevertheless, the obtained N : Pb profile shows more or less the same trend as revealed for the I : Pb ratio (Fig. 2e).
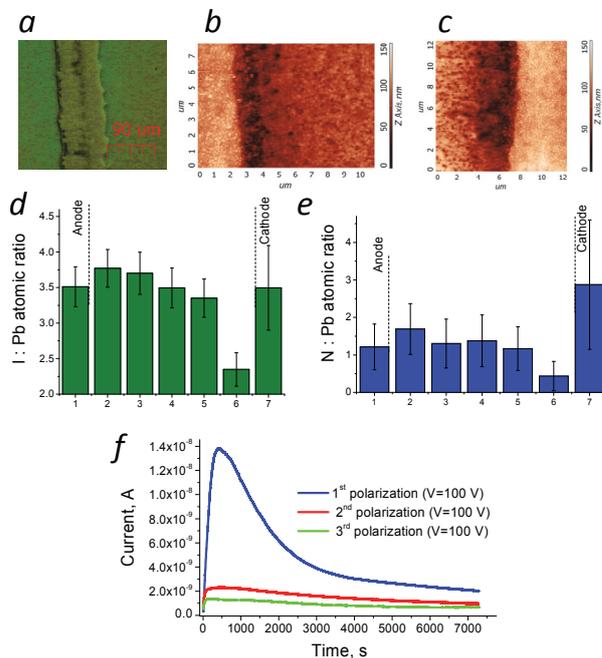

Figure 2. Optical microphotograph of the bottom-contact lateral device comprising MAPbI$_3$ perovskite film obtained ca. 5 min after polarization at 100 V within 2 h (a). Contact mode AFM images illustrating degradation of the perovskite layer nearby the anode (b) and cathode (c). Gradients in the I : Pb (d) and N : Pb (e) atomic ratios between anode and cathode as revealed by the EDXS analysis. Evolution of the device current *vs*. time during three successive polarization experiments performed in dark (f)

The overall set of the obtained experimental results proves that the perovskite MAPbI$_3$ films undergo decomposition under the applied electric field which is accompanied by transfer of some chemical species from one electrode to another. The anodic oxidation of the I$^-$ anions (free or incorporated in the structure of PbI$_3^-$) seems to liberate molecular iodine which can be trapped in the form of triiodide (I_3^-) or partially evolve from the films. At the same time, the cathode reaction might result in the reduction of the hydrogen ions (individual or incorporated in MA$^+$) to molecular hydrogen. Thus, the revealed decomposition actually represents electrolysis of the MAPbI$_3$ perovskite films producing I$_2$, H$_2$, CH$_3$NH$_2$ and PbI$_2$ (Scheme 1).

Anode process:

$$2\,(PbI_2)^*I^- \longrightarrow 2\,PbI_2 + I_2 + 2\,e^- \quad (1)$$

Cathode process:

$$2\,(CH_3NH_2)^*H^+ + 2\,e^- \longrightarrow 2\,CH_3NH_2 + H_2 \,(2)$$

Overall reaction:

$$2\,CH_3NH_3PbI_3 \xrightarrow{electrolysis} I_2 + H_2 + 2\,PbI_2 + 2\,CH_3NH_2$$

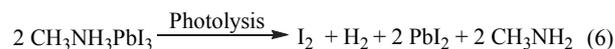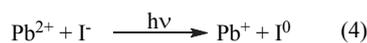Scheme 1. Decomposition of the MAPbI$_3$ under applied electric field

The obtained results prove clearly that $MAPbI_3$ perovskite represents an electrochemically active system with the mobile hydrogen (methylammonium) cations and iodine anions. The halogen ion conductivity of the inorganic perovskite-type complex led halides was reported at the beginning of 1980s.[14] More recently Yang et. al. have reported the observation of a strong iodine ion conductivity in the $MAPbI_3$ perovskite.[15] Surprisingly, motion of hydrogen ions in the hybrid $MAPbI_3$ and $FAPbI_3$ perovskites was not really considered by now.

In general, the role of the organic cations in hybrid perovskites is significantly underestimated. It is known that inorganic $CsPbI_3$ perovskite also forming a quasicubic structure does not work well in solar cells.[16] A gradual replacement of the organic cation (MA^+ or FA^+) with Cs^+ in the $APbI_3$ perovskite films results in a rapid deterioration of the solar cell performances when the cesium content goes above 20%.[17] These observations suggest that alkali metal cations (e.g. Cs^+) cannot play the same role as organic ammonium ions and support efficient operation of the perovskite absorbers in solar cells. On the other hand, it might be assumed that the presence of bare protons (not bonded to the amine molecules) in the perovskite lattice has a positive influence on the photovoltaic performance of the materials. Thus, it was noticed that introduction of HI and moisture to the FAI/PbI_2 precursor solution enhances the photovoltaic efficiency of the resulting films, though this effect is attributed to the improved film morphology.[6] More recently, FAI was mixed directly with $HPbI_3$ to produce the perovskite films demonstrating enhanced photovoltaic performances.[18] It is very likely that in both reported cases mobile H^+ ions replaced a part of the bulky FA^+ cations in the perovskite structure thus improving significantly proton conductivity of the system. We note that this assumption has no direct evidences at the moment and should be verified in the future.

Rather remarkable results were obtained while monitoring the evolution of the current flowing through the channel of the lateral device over time during the polarization experiment (Fig. 2f). One can see that the current starts to increase significantly immediately after applying the bias voltage and reaches the maximum within 7-10 min. The maximal current is 10-20 times higher compared to the initial value. The revealed effect was reproducible for all investigated top-contact and bottom-contact devices with except for some variation in the time when the maximal current is achieved (between 5 and 25 min). The observed remarkable increase in the current at the constant bias voltage is very uncommon for inorganic and organic semiconductor materials and reflects specific behavior of the $MAPbI_3$ perovskite films. We believe that partial oxidation of the I^- to I^0 results in the formation of the positively charged iodide ion vacancies $V_{I'}$ and local n-doping of the material. At the same time, partial reduction of H^+ to H^0 leads to the formation of the negatively charged proton vacancies $V_{H'}$ (p-doped region). Thus, generation of vacancies under the applied electric field improves significantly the charge transport characteristics of the material and also explains increase in the current at the beginning of the polarization experiment. This conclusion is also in line with the fact that the efficiency of the perovskite

solar cells can be often improved if they are polarized under constant bias voltage for some time prior the I-V measurement.[19] However, continuous polarization results in a massive degradation of the material according to Scheme 1 which suppresses charge transport and leads to decrease in the current observed at long polarization times (>30 min). The electrochemical degradation of the perovskite films is almost irreversible. Repeating the polarization experiment with the same device several times leads to a gradual decrease in the current flowing through the channel between two electrodes. Nevertheless, a general behavior of the system remains the same (Fig. 2f).

It is also important to consider a possibility of the photoinduced generation of the positively and negatively charge vacancies in the perovskite films. It was shown long time ago that PbI_2 crystals intercalated with amines undergo facile photolysis under relatively mild illumination conditions.[20] The investigated PbI_2+RNH_2 systems have rather strong similarity to the $MAPbI_3$ perovskites in terms of the chemical composition and structure. The observed photolysis effect was explained by the photoinduced electron transfer from I^- to Pb^{2+} resulting in the Pb^+ and I^0 (eq. 4 in Scheme 2).[20] This reaction is not very surprising since the I^+/I^0 photo(electro)chemistry has been well explored and utilized in the first-generation dye sensitized solar cells.[21]

$$Pb^{2+} + I^- \xrightarrow{h\nu} Pb^+ + I^0 \quad (4)$$

$$Pb^+ + H^+ \longrightarrow Pb^{2+} + H^0 \quad (5)$$

$$2\ CH_3NH_3PbI_3 \xrightarrow{Photolysis} I_2 + H_2 + 2\ PbI_2 + 2\ CH_3NH_2 \quad (6)$$

Scheme 2. Photodecomposition of $MAPbI_3$

The unstable monovalent Pb^+ ions might be converted back to Pb^{2+} to expense of the H^+ undergoing reduction to H^0 (eq. 5). This process seems to be favorable as it follows from the comparison of the standard potentials of the Pb^{2+}/Pb^0 (-0.13 V vs. SHE) and H^+/H^0 (0 V vs. SHE) couples in solution. However, one should keep in mind that environment of the Pb^+ (Pb^{2+}) and H^+ ions (e.g. their thermodynamic activities) in the perovskite crystals can alter significantly thermodynamics of these processes.

The overall chemical scheme of the photolysis process (eq. 6 in Scheme 2) is identical to the chemistry of the electrolysis process (eq. 3 in Scheme 1). Both schemes actually reflect electrochemical or photochemical splitting of the HI integrated in the perovskite structure to molecular hydrogen and iodine. It is known that this process does not require much energy and, therefore, most likely can occur under the specified conditions. The proposed photolysis scheme is supported by the formation of PbI_2 as one of the products of the $MAPbI_3$ photodecomposition under a concentrated sunlight (100 suns).[22]

A strong support of the presented here concept of the photochemical self-doping of the perovskite films has been reported recently by Gottesman et. al.[12] It was observed that lateral bottom-contact devices with the $MAPbI_3$ active layer demonstrate very slow rise in the current flowing between the electrodes within 1-2 min after switching the light. Authors

attributed the observed "slow photoconductivity" effect to some structural changes occurring in the perovskite films under illumination. We strongly believe that this effect is related to the photochemical self-doping. In order to verify this hypothesis, we reproduced experiment of Gottesman et. al.[12] We applied the light of the violet diode laser (ca. 12 mW, λ=405 nm) to the gap between the electrodes of the lateral device biased at 100 V and monitored the changes in the current. The device current showed a steep rise after switching on the light and then slow increase up to the maximum which is approached in ca. 20-30 seconds (Fig. S1). Afterwards, the current gradually decreased suggesting some degradation of the material. Further decrease in the current was observed while reproducing this experiment several times with the same device. The revealed trends resembled quite closely the device behavior during the polarization experiment (Fig. 2f).

Thus, the illumination of the perovskite films strongly facilitates the formation of the negatively charged hydrogen vacancies ($V_{H'}$) and positively charged iodine vacancies ($V_{I'}$) leading to the p-type and n-type doping of the material, respectively. Migration of these vacancies in the electric field seems to be responsible for the appearance of the hysteresis in the current-voltage characteristics of the perovskite solar cells and also explains "giant switchable photovoltaic effect" reported by Xiao et. al.[11] The photoinduced self-doping is corroborated by a strong photoconductivity of the $MAPbI_3$ films[12] and anomalous increase in their dielectric constant under illumination.[23]

In conclusion, we have shown that the $MAPbI_3$ perovskite should be considered as photochemically and electrochemically active dual-channel ion conductor rather than high-purity intrinsic semiconductor with low concentration of defects and ideal electronic characteristics. The proposed here self-doping chemistry explains why the perovskite solar cells behave as p-i-n devices and undergo reversible polarization in the applied electric field. It also agrees well with the electrophysical model proposed for the perovskite solar cells recently.[24]

It is also rather remarkable that the distribution of the defects in the perovskites in combination with their perfect 3D morphology with the interpenetrating networks of the hole-conducting (internal network of the organic cations) and the electron conducting (Pb-I cage) channels makes the perovskite solar cells very similar to the ideal bulk heterojunction architectures pursued by researchers for two decades previously. Further exploration of these exciting materials might result in the development of a new generation of highly efficient and sufficiently stable devices for solar energy conversion.

Notes and references

[a] *IPCP RAS, Semenov Prospect 1, Chernogolovka, 141432, Russia. Fax: +7 496515-5420; Tel: +7 496522 1418; E-mail: troshin2003@inbox.ru*

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1 N. J. Jeon, J. H. Noh, W. S. Yang, Y. C. Kim, S. Ryu, J. Seo and S. I. Seok, *Nature*, 2015, **517**, 476–480.

2 M. A. Green, K. Emery, Y. Hishikawa, W. Warta and E. D. Dunlop, *Prog. Photovolt.: Res. Appl.*, 2015, **23**, 1–9.

3 Q. Lin, A. Armin, R. C. R. Nagiri, P. L. Burn and P. Meredith, *Nat. Photon.*, 2014, **9**, 106–112; K. T. Butler, J. M. Frost and A. Walsh, *Mater. Horiz.*, 2015, **2**, 228–231

4 Q. Dong, Y. Fang, Y. Shao, P. Mulligan, J. Qiu, L. Cao and J. Huang, *Science*, 2015, **347**, 967–970.

5 D. Shi, V. Adinolfi, R. Comin, M. Yuan, E. Alarousu, A. Buin, Y. Chen, S. Hoogland, A. Rothenberger, K. Katsiev, Y. Losovyj, X. Zhang, P. A. Dowben, O. F. Mohammed, E. H. Sargent and O. M. Bakr, *Science*, 2015, **347**, 519–522.

6 G. E. Eperon, S. D. Stranks, C. Menelaou, M. B. Johnston, L. M. Herz, H. J. Snaith, *Energy Environ. Sci.* 2014, **7**, 982; Y. Chen, Y. Zhao and Z. Liang, *Chem. Mater.*, 2015, **27**, 1448–1451; Y.-J. Jeon, S. Lee, R. Kang, J.-E. Kim, J.-S. Yeo, S.-H. Lee, S.-S. Kim, J.-M. Yun and D.-Y. Kim, *Sci. Rep.*, 2014, **4**, 6953; H.-L. Hsu, C.-C. Chang, C.-P. Chen, B.-H. Jiang, R.-J. Jeng and C.-H. Cheng, *J. Mater. Chem. A*, 2015, **3**, 9271–9277; P.-W. Liang, C.-Y. Liao, C.-C. Chueh, F. Zuo, S. T. Williams, X.-K. Xin, J. Lin and A. K.-Y. Jen, *Adv. Mater.*, 2014, **26**, 3748–3754.

7 D. K. Susarova, N. P. Piven, A. V. Akkuratov, L. F. Frolova, M. S. Polinskaya, S. A. Ponomarenko, S. D. Babenko, P. A. Troshin, *Chem. Comm.*, 2015, **51**, 2239-2241

8 J. M. Frost, K. T. Butler, F. Brivio, C. H. Hendon, M. van Schilfgaarde and A. Walsh, *Nano Lett.*, 2014, **14**, 2584–2590; K. T. Butler, J. M. Frost and A. Walsh, *Energy Environ. Sci.*, 2015, **8**, 838–848; A. Walsh, *J. Phys. Chem. C*, 2015, **119**, 5755–5760.

9 W.-J. Yin, T. Shi and Y. Yan, Appl. Phys. Lett., 2014, 104, 063903; J. Kim, S.-H. Lee, J. H. Lee and K.-H. Hong, *J. Phys. Chem. Lett.*, 2014, **5**, 1312–1317; Q. Wang, Y. Shao, H. Xie, L. Lyu, X. Liu, Y. Gao and J. Huang, *Appl. Phys. Lett.*, 2014, **105**, 163508.

10 A. Walsh, D. O. Scanlon, S. Chen, X. G. Gong and S.-H. Wei, *Angew. Chem. Int. Ed*, 2015, **54**, 1791–1794.

11 Z. Xiao, Y. Yuan, Y. Shao, Q. Wang, Q. Dong, C. Bi, P. Sharma, A. Gruverman and J. Huang, *Nat. Mater.*, 2014, **14**, 193–198.

12 R. Gottesman, E. Haltzi, L. Gouda, S. Tirosh, Y. Bouhadana, A. Zaban, E. Mosconi and F. De Angelis, *J. Phys. Chem. Lett.*, 2014, **5**, 2662–2669.

13 B. R. Vincent, K. N. Robertson, T. S. Cameron and O. Knop, *Canad. J. Chem.* 1987, **65**, 1042–1046.

14 J. Mizusaki, K. Arai and K. Fueki, *Sol. State Ionics*, 1983, **11**, 203–211.

15 T.-Y. Yang, G. Gregori, N. Pellet, M. Grätzel and J. Maier, *Angew. Chem. Int. Ed.,* 2015, DOI: 10.1002/anie.201500014

16 L. Protesescu, S. Yakunin, M. I. Bodnarchuk, F. Krieg, R. Caputo, C. H. Hendon, R. X. Yang, A. Walsh and M. V. Kovalenko, *Nano Lett.*, 2015, 150414154048008.

17 H. Choi, J. Jeong, H.-B. Kim, S. Kim, B. Walker, G.-H. Kim and J. Y. Kim, *Nano Energy*, 2014, **7**, 80–85.

18 F. Wang, H. Yu, H. Xu and N. Zhao, *Adv. Funct. Mater.*, 2015, **25**, 1120–1126.

19 S. Ryu, J. Seo, S. S. Shin, Y. C. Kim, N. J. Jeon, J. H. Noh and S. I. Seok, *J. Mater. Chem. A*, 2015, **3**, 3271–3275; S. N. Habisreutinger, T. Leijtens, G. E. Eperon, S. D. Stranks, R. J. Nicholas and H. J. Snaith, *Nano Lett.* 2014, **14**, 5561–5568.

20 G. I. Gurina, V. D. Evtushenko, A. Y. Kobyakov and V. M. Koshkin, *Theor. Exp. Chem.*, 1986, **21**, 718–719.

21 G. Boschloo and A. Hagfeldt, *Acc. Chem. Res.*, 2009, **42**, 1819–1826.

22 R. K. Misra, S. Aharon, B. Li, D. Mogilyansky, I. Visoly-Fisher, L. Etgar and E. A. Katz, *J. Phys. Chem. Lett.*, 2015, **6**, 326–330.

23 E. J. Juarez-Perez, R. S. Sanchez, L. Badia, G. Garcia-Belmonte, Y. S. Kang, I. Mora-Sero and J. Bisquert, *J. Phys. Chem. Lett.*, 2014, **5**, 2390–2394.

24 K. Miyano, M. Yanagida, N. Tripathi and Y. Shirai, *Appl. Phys. Lett.*, 2015, **106**, 093903.