ELSEVIER

Check for
updates

Theory of light-induced degradation in perovskite solar cells

Hamid Shahivandi [a], Majid Vaezzadeh [a], Mohammadreza Saeidi [b,*]

[a] Department of Solid State Physics, Faculty of Physics, K. N. Toosi University of Technology, Tehran, Iran
[b] Department of Physics, Faculty of Basic Sciences, Shahed University, Tehran, Iran

ARTICLE INFO

ABSTRACT

One of the fundamental challenges that have prevented practical use of the perovskite solar cell is the current degradation in exposure conditions, causing instability of the power conversion efficiency. We present here a theory for this current degradation in perovskite solar cells. Many researchers attribute this degradation to the vacancies migration in the perovskite layer. But there are two fundamental ambiguities in the theories presented for the ion migration process. First, according to the assumptions of these theories, this vacancy migration to the sides of the perovskite layer should also happen in dark conditions, while this occurs only in exposure conditions. Second, according to the assumptions of these theories, the degraded solar cell should not be recovered in dark conditions, while recovery takes place in dark conditions. The approach we present in this paper provides a good understanding of the processes of degradation and recovery in perovskite solar cells, as well as resolves these ambiguities.

1. Introduction

Perovskite as a light absorber have attracted a lot of attention in last decade, and many experimental and theoretical studies have been done on perovskite for using in solar cells [1–11] after application for the first time by Kojima et al. [12] as a light absorber in dye-sensitized solar cells. In Solid-state perovskite solar cell (PSC) [13], perovskite is used as the main absorber matter because it has properties such as high absorption coefficient, high mobility of electron-hole pair, and low recombination rate of electron-hole pair, that are essential for solar cells [14]. Using these features, researchers have achieved perovskite solar cells with a power conversion efficiency of more than 22% in last decade [15,16]. Also, simple construction process and low production cost are another characteristics of perovskite solar cells [16], compared to silicon solar cells.

But along with these positive features, PSCs are facing fundamental challenges that to date inhibited commercial production and practical use of these solar cells. The main challenges ahead are (i) Toxicity of the materials used in the cell (such as lead) [17], (ii) Instability of the structure under environmental factors including light, temperature, and humidity [16]. Therefore, a large part of the research work in perovskite solar cells focuses on removing these two main obstacles.

One of the main problems of PSCs is the degradation of energy conversion efficiency over the exposure time. According to experimental

results, when PSC is exposed to light, its initial energy conversion efficiency is the highest possible amount and decreases over time to a small value. If this degraded cell is stored in the dark, after a specific time (depending on cell structure and environmental conditions), it restores to the initial state and reaches the initial efficiency [18–22]. This paper aims to present an appropriate theory to explain the physics of the "light-induced degradation" and "recovery under dark condition" processes in perovskite solar cells. In most of the works that have already been done to understand the physics of the light-induced degradation and recovery in the dark condition in perovskite solar cells, researchers have attributed these processes to the migration of ions through vacancies due to the effect of the built-in electric field [18–20]. But a complete theory to explain the physics of these processes has not been presented. There are two fundamental ambiguities in explaining degradation and recovery processes that previous theories cannot solve them. The first ambiguity is that in dark conditions and before exposure, no degradation occurs in the perovskite solar cell, so the vacancies will not migrate; however, the vacancies and the built-in electric field are still present in the dark condition. As the second ambiguity, when the solar cell is stored in dark conditions to be recovered, the vacancies are propagated in the perovskite layer, and the cell returns to its original state, while no change in the built-in electric field has occurred.

In this work, we present the theory of light-induced efficiency degradation in $CH_3NH_3PbI_3$ perovskite solar cells using experimental

---

* Corresponding author.
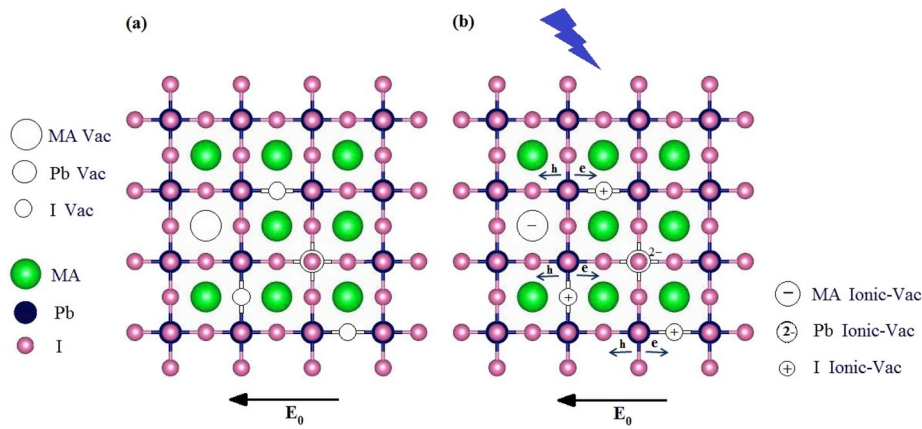 E-mail addresses: Saeidi.mr@gmail.com, m.saeidi@shahed.ac.ir (M. Saeidi).

Fig. 1. A schematic diagram of the $CH_3NH_3PbI_3$ perovskite. a) Vacancies in dark conditions. b) Vacancies in exposure conditions.

results obtained by the researchers [18–22]. In addition to helping to understand the processes of degradation and recovery, this theory also solves the ambiguities mentioned above.

2. Theory of light-induced current degradation

Light-induced current degradation issue has been discussed in many articles [18–22]. In most of these articles, light-induced degradation has been attributed to the migration of vacancies in the perovskite layer. After exposure, to restore the cell to the initial performance condition and eliminate the current degradation, it is stored in the dark. It means that by interrupting the exposure, the vacancies return to the perovskite layer volume, and the solar cell restores to the initial conditions. Some researchers have attributed charges to these vacancies and have assumed that these ionic vacancies are affected by the built-in electric field [18]. The ionic vacancies migrate under the influence of the built-in electric field to the sides of the perovskite layer, which lead to attenuation of the built-in electric field.

But there are two fundamental ambiguities in the physics presented for this phenomenon: (i) If the vacancy migration is related to the built-in electric field, then it should occur in dark conditions too, and thus degradation of efficiency should happen under any circumstances, while the degradation occurs only in exposure conditions; (ii) In the dark, when the cell is restoring, the built-in electric field is still present and no new force is applied to the vacancies to separates them from the perovskite surfaces and returns them to the volume of the perovskite layer.

Here the physics of degradation and restoring processes is expressed in such a way that the mentioned ambiguities will be resolved. The prepared $CH_3NH_3PbI_3$ perovskite layer has defects in its crystalline lattice including vacancies, impurities, etc. which are dispersed uniformly in the layer. When a vacancy is formed in a unit cell of the $CH_3NH_3PbI_3$ perovskite crystal, for example, an iodine vacancy, the complete unit cell comes in a combination of a $CH_3NH_3PbI_2$ molecule and a vacancy of iodine atom, which is electrically neutral. But there is one electron in this incomplete unit cell that is responsible for bonding the absent atom to the unit cell, and if the iodine atom were present in the vacant position, this bonding electron would ionize the iodine atom. The binding energy of this electron is lower than that for other electrons at complete unit cells. Similarly, for positive ions, vacancies form with bonding holes. So, for lead and methylammonium which are positive ions in $CH_3NH_3PbI_3$ perovskite, their vacancies form with two and one bonding holes, respectively. This bonding electrons and holes are excited with lower energy than the perovskite band gap energy.

Under equilibrium conditions and without exposure, vacancies are electrically neutral (because they are vacancies of iodine atom (I) and methylammonium (CH_3NH_3) molecule), and bonding electrons and

holes belong to their source atoms or molecules. These neutral vacancies are dispersed uniformly throughout the volume of the perovskite layer. So the perovskite structure is electrically neutral and built-in electric field cannot affect the neutral vacancies (Fig. 1(a)). When perovskite solar cell is exposed to light, two kinds of electron-hole pair are excited: (i) electron-hole pairs from the complete part of the perovskite lattice which are excited by photons with energy of $E_{ph} \geq E_{gap}$; (ii) electron-hole pairs from the incomplete part of the perovskite lattice which are even excited with energies less than the band gap energy. The second category of electron-hole pairs, which belong to absent atoms or molecules and ionize them, are represented in Fig. 1(b) with "e" and "h" symbols respectively. When these electron-hole pairs are excited, then the vacancies are no longer neutral, and we can assume them as "ionic vacancies" (Fig. 1(b)).

By exposing the solar cell to light, the bonding electrons and holes are excited, and the vacancies are ionized (because now they are vacancies of iodine ion (I^-) and methylammonium ion ($CH_3NH_3^+$)), which we call them "quasi-ions". Therefore, the quasi-ions migrate to the sides of the perovskite layer under the built-in electric field. The iodine quasi-ions (ionized vacancies of iodine) with positive charge move in the direction of the built-in electric field and the MA quasi-ions (ionized vacancies of MA) move in the opposite direction of the built-in electric field. So, these accumulated quasi-ions on the sides of the perovskite layer forms a new electric field that its direction is opposite to that of the built-in electric field. This new electric field grows to some extent to completely neutralize the built-in electric field and completely degrade the solar cell.

2.1. Degradation of the built-in field

If the internal energy of the ions is equal to or greater than their migration activation energy, these ions can jump to the adjacent vacancies. We considered vacancies as quasi-particles that migrate in the perovskite lattice, instead of moving ions in empty positions. In the dark conditions, these quasi-particles are electrically neutral, so their movement is random, and their net flow in the structure is equal to zero. Once the perovskite structure containing the vacancies is exposed to light radiation, the bonding electrons and holes are released, and as a result, their vacancies are ionized. So, the motion of these ionized quasi-particles (quasi-ions) is no longer random, and their displacement is in line with the built-in electric field of the cell. With regards to the migration activation energy of the $CH_3NH_3PbI_3$ vacancies ($E_a(I^-) = 0.58\ eV$, $E_a(Pb^{2+}) = 2.31\ eV$, $E_a(CH_3NH_3^-) = 0.84\ eV$), the displacement of the lead vacancies is negligible, so only the migration of iodine and methylammonium vacancies is considered [7]. Therefore, iodine quasi-ions with a positive charge move in the direction of the built-in electric field and methylammonium quasi-ions with a negative charge
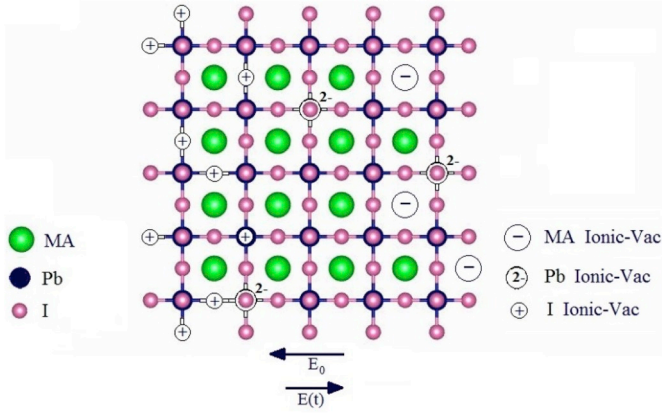
Fig. 2. A schematic of the accumulation of quasi-ions on the sides of the $CH_3NH_3PbI_3$ perovskite layer, which leads to the formation of a new electric field.

move opposite to it. Over time, positive and negative quasi-ions accumulate on the p-side and n-side of the cell, respectively. We assume that iodine and methylammonium quasi-ions form two nonconducting, infinite plane on the sides of the perovskite layer with uniform surface charge density σ_1 and σ_2 respectively. The magnitude of these charge densities increases with exposure time (Fig. 2).

A new electric field appears across the perovskite layer due to the formation of the charge planes. Using Gauss's law, we can write the magnitude of this new electric field ($E_1(t)$) as follows:

$$E_1(t) = \frac{\sigma_1(t)}{2\varepsilon} + \frac{\sigma_2(t)}{2\varepsilon} \tag{1}$$

where ε is the permittivity of the perovskite layer. We can define σ_1 and σ_2 as follows:

$$\sigma_1(t) = \frac{Q_I(t)}{A} \tag{2a}$$

$$\sigma_2(t) = \frac{Q_{MA}(t)}{A} \tag{2b}$$

where A is the perovskite layer cross-section, and Q_I and Q_{MA} are the magnitudes of the accumulated charges on sides of the layer by iodine and methylammonium vacancies, respectively. Whereas the direction of the new electric field is in the opposite of the built-in electric field (E_0), so the magnitude of the total electric field is:

$$E(t) = E_0 - E_1(t) \tag{3}$$

To obtain this new electric field, we solve the equations of motion for these quasi-ions:

$$m_I^* \frac{dv_I}{dt} = - |q_I| E(t) \tag{4a}$$

$$m_{MA}^* \frac{dv_{MA}}{dt} = - |q_{MA}| E(t) \tag{4b}$$

where v_I (v_{MA}), m_I^* (m_{MA}^*), and q_I (q_{MA}) are the average velocity across the perovskite layer, the effective mass, and the charge number, respectively for the iodine (methylammonium) quasi-ion. In this theory, we assume that the quasi-ions are free particles (with an effective mass of m^*), which move under the influence of the electric field. The negative signs indicate the decrease of the electric field over time, which causes the average velocities to decrease with time. Whereas $|q_I| = |q_I| = e$, so the second sides of the (4a) and (4b) equations will be equal and we will have:

$$m_I^* \frac{dv_I}{dt} = m_{MA}^* \frac{dv_{MA}}{dt} \tag{5}$$

Assuming that the effective masses are constant, we obtain the following relation:

$$m_I^* v_I = m_{MA}^* v_{MA} \tag{6}$$

By differentiating both sides of the (4a) and (4b) equations with respect to time:

$$m_I^* \frac{d^2 v_I}{dt^2} = \frac{q_I}{2\varepsilon A} \left(\frac{dQ_I}{dt} + \frac{dQ_{MA}}{dt} \right) \tag{7a}$$

$$m_{MA}^* \frac{d^2 v_{MA}}{dt^2} = \frac{q_{MA}}{2\varepsilon A} \left(\frac{dQ_I}{dt} + \frac{dQ_{MA}}{dt} \right) \tag{7b}$$

To define the time dependence of accumulated charges on both sides, we assume that the quasi-ions with densities of n_I and n_{MA}, and with average velocities of v_I and v_{MA} (as defined above), pass through the cross-section A of the perovskite layer. Therefore, the differential of accumulated charges on each side of the layer is defined as:

$$dQ_I = e\, n_I v_I(t)\, A\, dt \tag{8a}$$

$$dQ_{MA} = e\, n_{MA} v_{MA}(t)\, A\, dt \tag{8b}$$

By substituting these expressions in equation (7a) and using equation (6), we obtain the following differential equation for the velocity of the iodine quasi-ions:

$$\frac{d^2 v_I(t)}{dt^2} = \frac{e^2}{2\varepsilon} \left[\frac{n_I}{m_I^*} + \frac{n_{MA}}{m_{MA}^*} \right] v_I(t) \tag{9}$$

which the solution to this equation is as follows:

$$v_I(t) = a\, e^{\alpha t} + b\, e^{-\alpha t} \tag{10}$$

where

$$\alpha^2 = \frac{e^2}{2\varepsilon} \left[\frac{n_I}{m_I^*} + \frac{n_{MA}}{m_{MA}^*} \right] \tag{11}$$

By applying the boundary condition of $t \to \infty$, the solution (10) must be finite, so we must put $a = 0$. Also by applying the boundary condition of $t = 0$, the solution (10) must be equal to $v_I(0)$, which is the average velocity of the iodine quasi-ions just before the formation of the new electric field $E_1(t)$, in other words, is the average velocity due to the built-in field E_0, so:

$$v_I(t) = v_I(0)\, e^{-\alpha t} \tag{12}$$

By substituting this expression in equation (4a), we can obtain the total electric field:

$$E(t) = \frac{m_I^* v_I(0)\, \alpha}{e}\, e^{-\alpha t} \tag{13}$$

By applying the boundary condition of $t = 0$, where $E(t = 0) = E_0$, we can obtain the relation between $v_I(0)$ and E_0 as follow:

$$v_I(0) = \frac{e\, E_0}{m_I^* \alpha} \tag{14}$$

So, the final relations for velocities of the iodine and methylammonium quasi-ions are:

$$v_I(t) = \frac{E_0}{m_I^*} \sqrt{\frac{2\varepsilon}{(n_I / m_I^* + n_{MA} / m_{MA}^*)}}\, e^{-\alpha t} \tag{15}$$

$$v_{MA}(t) = \frac{E_0}{m_{MA}^*} \sqrt{\frac{2\varepsilon}{(n_I/m_I^* + n_{MA}/m_{MA}^*)}} \; e^{-\alpha \, t} \qquad (16)$$

Also, the final relation for the total electric field across the $CH_3NH_3PbI_3$ perovskite layer is as follows:

$$E(t) = E_0 \, e^{-\alpha \, t} \qquad (17)$$

The relation (17) indicates that the quasi-ions accumulation in the sides of the perovskite layer causes the electric field across the layer decreases exponentially over time, which leads to a reduction in the efficiency of the electron-hole separation. To analyze the result of the proposed theory (relation (17)), the values of the parameters including the built-in electric field (E_0), the absolute permittivity of the perovskite layer (ε), the effective mass of the quasi-ions (m_I^* and m_{MA}^*), and the density of the quasi-ions (n_I and n_{MA}) must be specified.

Built-in electric field: the difference between the work function of the two materials on both sides of the perovskite layer creates an inherent potential, which results in the formation of the built-in electric field, so it is defined as follows:

$$E_0 = \frac{V_0}{w} \qquad (18)$$

where V_0 is the inherent potential, and w is the thickness of the perovskite layer.

Absolute permittivity: for $CH_3NH_3PbI_3$ perovskite, the relative permittivity ε_r for optical frequencies is 6.5 [23], therefore, the absolute permittivity is $\varepsilon = \varepsilon_0 \varepsilon_r = 5.755 \times 10^{-11} \, C^2/N \, m^2$.

Effective mass: whereas, in reality, ions displace in the crystal lattice, not the vacancies, so we define the effective mass of the quasi-ions as their corresponding free ion mass. For example, we define the effective mass of iodine quasi-ion as the mass of a free iodine ion. Diffusion coefficient represents the rate of propagation of a species in a material. Species that have high diffusion coefficient can easily move in the lattice structure and feel low propagation resistance, on the other hand, if the propagation resistance is low, then a smaller effective mass is given to the species. Therefore, we use this correlation to define the effective mass of the quasi-ions. Using the Arrhenius Equation for the diffusion coefficient, $D = D_0 \exp(-E_a/RT)$, we define the following expression for the effective mass:

$$m^* = \frac{m}{e^{-(E_a + U_f)/RT}} \qquad (19)$$

where E_a is the activation energy of the species [18] (the energy needed to overcome the propagation resistance of the structure to the motion of the ion), R is the gas constant, m is the mass of the corresponding ion, and U_f is the vacancy formation energy, energy needed to displace an ion from the volume to the surface of the structure. The amount of E_a depends on the immigrant ion dimensions and the structure of the crystal lattice in which it moves. We have used the experimental results of K. Domanski et al. [20] to obtain an experimental value for U_f. According to their results, the first series of iodine quasi-ions arrive at one side of the perovskite layer in time scales shorter than $10^2 s$, and the first series of methylammonium quasi-ions arrive at another side of the layer in time scales of $10^3 s$. Because for these first series the new electric field is negligible compared to the built-in electric field, so it can be assumed that these quasi-ions move under a constant electric force with the acceleration of $a = eE_0/m^*$ and pass through the thickness of the perovskite layer. Therefore, by using the relation $w = 1/2 \, a \, t^2$, effective mass values can be estimated as follows:

$$m^* = \frac{e \, E_0 t}{2 \, w} = \frac{e V_0 \, t}{2 \, w^2} \qquad (20)$$

The results obtained from this relation indicate that the amounts of the vacancy formation energy for iodine and methylammonium quasi-

ions are $U_f^I \approx 0.775 \, eV$ and $U_f^{MA} \approx 0.667 \, eV$, respectively.

2.2. Theory of perovskite solar cell recovery in dark conditions

By storing the degraded cell in dark conditions, it recovers to its initial efficiency after a while. Under dark conditions, no new photons are absorbed by the perovskite layer, so no new electron-hole pair is formed. On the other hand, excited electrons recombine with holes, and as a result, the vacancies are recovered to the original electrically neutral state. Therefore, there are two types of electrically neutral vacancies accumulated on both sides of the perovskite layer. The built-in electric field will no longer affect these neutral vacancies. This difference in the density across the layer causes vacancies to diffuse from the region with higher concentration to the region with lower concentration. After a while, vacancies distribute uniformly throughout the perovskite layer, and the cell is recovered to the initial conditions.

We assume that, with sufficient exposure time, all the vacancies accumulate in two thin layers of thickness δ on the sides of the perovskite layer. By integrating both sides of the relations (8a) and (8b) with respect to time, the final densities of the accumulated vacancies are obtained as follows:

$$n_{I\delta} = \frac{n_{I0} \, v_I(0)}{\alpha \, \delta} \qquad (21)$$

$$n_{MA\delta} = \frac{n_{MA0} \, v_{MA}(0)}{\alpha \, \delta} \qquad (22)$$

where n_{I0} and n_{MA0} are uniform vacancy densities for iodine and methylammonium vacancies, respectively in dark conditions, also $n_{I\delta}$ and $n_{MA\delta}$ are uniform vacancy densities of iodine and methylammonium vacancies, respectively in full exposure conditions in the layers with a thickness of δ.

3. Results and discussion

The purpose of this work was to provide a suitable theory for describing the physics of the processes of "light-induced degradation" and "recovery under dark conditions" for perovskite solar cells. Here, we considered the migration of vacancies instead of the migration of ions. According to the theory presented in this paper, in dark conditions, all unit cells, including cells containing vacancy, are electrically neutral. A unit cell containing a vacancy, for example, an iodine-vacancy, has a major difference with a complete unit cell. In the incomplete unit cell, in addition to the vacancy, there is an electron that is responsible for bonding the absent atom to the unit cell. We assumed that this electron belongs to the vacancy. This electron, which we called the "bonding electron", plays a key role in the processes of degradation and recovery in the perovskite solar cells. In dark conditions, the bonding electron belongs to the incomplete cell, so the incomplete cell and its vacancy are electrically neutral. Therefore, under dark conditions, the built-in electric field of the solar cell will not affect these neutral vacancies. When the solar cell is exposed to light, these bonding electrons are excited along with the other electrons, forming electron-hole pairs. Therefore, the vacancies lose their electrons and become ionized vacancies, which we called them "quasi-ions". These quasi-ions are affected by the built-in electric field and move to the sides of the perovskite layer. These accumulated quasi-ions form a new electric field that its direction is opposite to the direction of the built-in field. The built-in field separates the electron-hole pairs in the solar cell, and its existence is vital for solar cells. Therefore, this new electric field gradually weakens the built-in electric field severely and thus degrades the power conversion efficiency.

Based on the experimental findings of the researchers, by placing the degraded perovskite solar cell in dark conditions, it is restored to its initial state. Our theory well explains the physics of this recovery
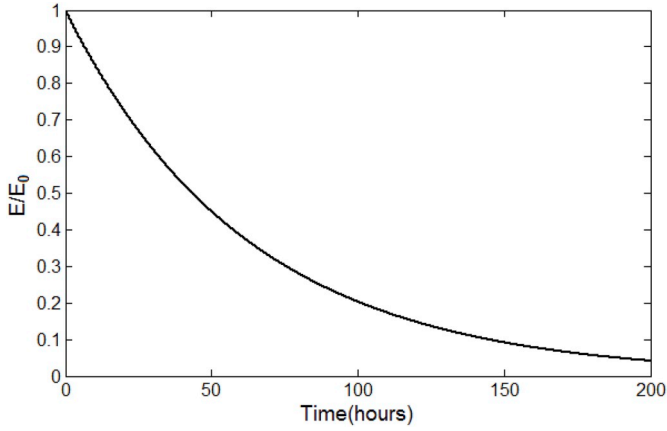
Fig. 3. Time dependence of the total electric field across the $CH_3NH_3PbI_3$ perovskite layer under exposure conditions.

process. In dark conditions, the process of producing new electron-hole pairs is stopped, and the generated pairs are recombined. Therefore, the vacancies will regain their electrons and become electrically neutral again, and thus the built-in electric field will no longer affect them. Subsequently, due to the vacancies density gradient on the perovskite layer, these vacancies diffuse uniformly throughout the perovskite layer and the cell returns to its initial state.

Using the proposed model in the previous section for the formation and displacing of the quasi-ions in perovskite layer, it is possible to resolve the ambiguities in cell degradation and recovery processes. The results of the proposed model show that by starting of exposure the total electric field decreases across the perovskite and eventually tends to zero. Fig. 3 shows the total electric field changes over time for a FTO glass/TiO$_2$/CH$_3$NH$_3$PbI$_3$/Spiro-OMeTAD/Au solar cell with perovskite thickness of 300 nm, iodine vacancy density of $n_I = 10^{15}\ m^{-3}$, and at a temperature of 300 K. The predictions of the presented model are in good agreement with the experimental results [19,22]. Fig. 3 shows that the total built-in electric field, which is responsible for the electron-hole pair separation, decreases exponentially with the exposure time. Thus, our model confirms that the energy conversion efficiency of the perovskite solar cell degrades exponentially.

By applying an external bias to the sides of the solar cell, an external electric field (E_{ext}) is also added to the total electric field. So this external electric field is added to the built-in electric field as follows:

$$E_0' = E_0 + E_{ext} = E_0 - \frac{V_{ext}}{w} \tag{23}$$

where E_0 and E_0' are the initial electric field without external bias (built-in electric field) and with external bias respectively, and V_{ext} is the applied external bias. The V_{ext} value is positive for forward bias and negative for reverse bias. Applying forward bias causes the initial total electric field to decrease, so the migration of the quasi-ions is carried out under a smaller electric force. This causes the vacancies to migrate with a lower rate, and as a result, the built-in electric field (Eq. (1)) degrade at a lower rate.

To investigate the effect of external bias on perovskite solar cell degradation, we studied the temporal dependence of the number of accumulated quasi-ions under different biases. According to Eq. (1), the amount of the surface charge density accumulated on the sides of the perovskite layer determines the magnitude of the new electric field ($E_1(t)$). The number of quasi-ions accumulated on the sides of the perovskite layer can be obtained by using Eqs. (8), (12) and (14), as follows:

$$N_I = \frac{n_I q_I A E_0}{m_I \alpha} \left(1 - e^{-\alpha t}\right) \tag{24}$$

$$N_{MA} = \frac{n_{MA} q_{MA} A E_0}{m_{MA} \alpha} \left(1 - e^{-\alpha t}\right) \tag{25}$$

where N_I and N_{MA} are the number of accumulated iodine and methylammonium quasi-ions, respectively. Fig. 4 shows the time dependence of the number of iodine (Fig. 4(a)) and methylammonium (Fig. 4(b)) quasi-ions per unit area, accumulated on sides of the perovskite layer of a FTO glass/TiO$_2$/CH$_3$NH$_3$PbI$_3$/Spiro-OMeTAD/Au solar cell for different applied biases.

It is clear from Fig. 4 that applying forward bias reduces the rate of accumulation and the final number (in saturation state) of quasi-ions relative to that without applying bias. Therefore, in forward bias condition, the magnitude of the new field of $E_1(t)$, resulting from accumulated quasi-ions, decreases compared to non-bias condition. In the non-bias condition, the quasi-ion accumulation on the sides of the perovskite layer will continue until the new electric field of $E_1(t)$ completely covers the built-in electric field. But in forward bias condition, a part of the built-in electric field is covered by the external electric field, and the new electric field will cover the rest. So, the quasi-ions accumulate on the sides until the electric field of $E_0 - E_{ext}$ is covered. When the $E_0 - E_{ext}$ electric field is completely covered, the cell will degrade completely. In this condition, if the bias is removed, a part of the built-in electric field, equal to E_{ext}, will be left uncovered. So, the cell will start working again, and the quasi-ions will start to migrate until this part of the built-in electric field is also covered completely.

As can be concluded from Fig. 4, applying reverse bias has an opposite effect compared to forward bias. Applying reverse bias
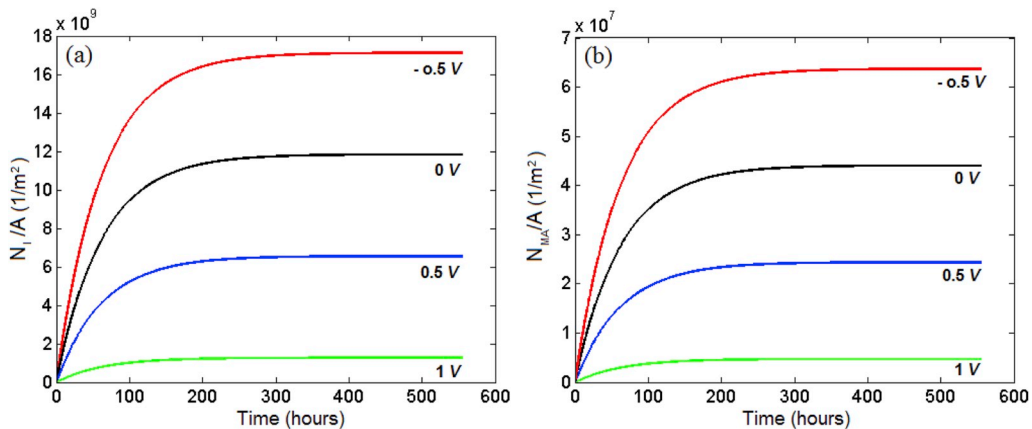

Fig. 4. Time dependence of the number of (a) iodine and (b) methylammonium quasi-ions accumulated per unit area of the perovskite layer under different applied biases of -0.5, 0, 0.5, 1 V.

increases the rate of migration of quasi-ions and their final number per unit area. Because in this condition, the external electric is in the same direction as the built-in electric field. So, under reverse bias conditions, the magnitude of the new field of $E_1(t)$ increases relative to non-bias conditions. In this condition, the number of quasi-ions accumulated on the sides of the perovskite layer is higher than that needed to cover and neutralize the built-in electric field. Therefore, under reverse bias, the new electric field of $E_1(t)$ is larger than the built-in electric field, and the solar cell degrades completely. By removing the reverse bias, the quasi-ions over what is needed to cover the built-in electric field, defuse into the perovskite layer because of the density gradient, and the magnitude of the new electric field will be equal to the built-in electric field $(E_1(t) = E_0)$.

The results of the proposed theory show that applying bias changes the vacancy migration rate and their final number accumulated at the sides of the perovskite layer. It means that the applying bias changes the degradation behavior of the perovskite solar cell, which is also confirmed by experimental works [22].

In conclusion, we proposed a theory for the processes of light-induced degradation of perovskite solar cells and their recovery under dark conditions. This theory is based on the migration of ions (or equivalently vacancies) and resolves the fundamental ambiguities in earlier approaches.

Author contributions section

Hamid Shahivandi: Conceptualization, Writing – Original Draft, Methodology.

Majid Vaezzadeh: Supervision, Validation.

Mohammadreza Saeidi: Conceptualization, Supervision, Writing – Review & Editing, Methodology.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

[1] T. Zhou, M. Wang, Z. Zang, L. Fang, Stable dynamics performance and high efficiency of ABX$_3$-type super-alkali perovskites first obtained by introducing H$_5$O$_2$ cation, Adv. Energy Mater. 9 (2019), 1900664.

[2] H. Zhang, X. Qiao, Y. Shen, T. Moehl, S.M. Zakeeruddin, M. Grätzel, M. Wang, Photovoltaic behavior of lead methylammonium triiodide perovskite solar cells down to 80 K, J. Mater. Chem. 3 (2015) 11762–11767.

[3] X. Zeng, T. Zhou, C. Leng, Z. Zang, M. Wang, W. Hu, X. Tang, S. Lu, L. Fang, M. Zhou, Performance improvement of perovskite solar cells by employing a CdSe quantum dot/PCBM composite as an electron transport layer, J. Mater. Chem. 5 (2017) 17499–17505.

[4] B.J. Foley, D.L. Marlowe, K. Sun, W.A. Saidi, L. Scudiero, M.C. Gupta, J.J. Choi, Temperature dependent energy levels of methylammonium lead iodide perovskite, Appl. Phys. Lett. 106 (2015), 243904.

[5] T. Zhou, M. Wang, Z. Zang, X. Tang, L. Fang, Two-dimensional lead-free hybrid halide perovskite using superatom anions with tunable electronic properties, Sol. Energy Mater. Sol. Cells 191 (2019) 33–38.

[6] T. Zhou, Y. Zhang, M. Wang, Z. Zang, X. Tang, Tunable electronic structures and high efficiency obtained by introducing superalkali and superhalogen into AMX3-type perovskites, J. Power Sources 429 (31) (2019) 120–126.

[7] B. Yang, M. Wang, X. Hu, T. Zhou, Z. Zang, Highly efficient semitransparent CsPbIBr2 perovskite solar cells via low-temperature processed In2S3 as electron-transport-layer", Nano Energy 57 (2019) 718–727.

[8] N. Mohammadian, A. Moshaii, A. Alizadeh, S. Gharibzadeh, R. Mohammadpour, Influence of perovskite morphology on slow and fast charge transport and hysteresis in the perovskite solar cells, J. Phys. Chem. Lett. 7 (22) (2016) 4614–4621.

[9] H.J. Snaith, Perovskites: the emergence of a new era for low-cost, high-efficiency solar cells, J. Phys. Chem. Lett. 4 (21) (2013) 3623–3630.

[10] M.A. Green, A. Ho-Baillie, H.J. Snaith, The emergence of perovskite solar cells, Nat. Photonics 8 (2014) 506–514.

[11] J. Burschka, N. Pellet, S.J. Moon, R. Humphry-baker, P. Gao, M.K. Nazeeruddin, M. Grätzel, Sequential deposition as a route to high-performance perovskite-sensitized solar cells, Nature 133 (2013) 316–319.

[12] A. Kojima, K. Teshima, Y. Shirai, T. Miyasaka, Organometal halide perovskites as visible- light sensitizers for photovoltaic cells, J. Am. Chem. Soc. 131 (2009) 6050–6051.

[13] H.S. Kim, C.R. Lee, J.H. Im, K.B. Lee, T. Moehl, A. Marchioro, S.J. Moon, R. Humphry-Baker, J.H. Yum, J.E. Moser, M. Grätzel, N.G. Park, Lead iodide perovskite sensitized all-solid-state submicron thin film mesoscopic solar cell with efficiency exceeding 9%, Sci. Rep. 2 (2012) 591.

[14] I. Mesquita, L. Andrade, A. Mendes, Perovskite solar cells: materials, configurations and stability, Renew. Sustain. Energy Rev. 82 (2018) 2471–2489.

[15] W.S. Yang, B.-W. Park, E.H. Jung, et al., "Iodide management in formamidinium-leadhalide–based perovskite layers for efficient solar cells", Science 356 (6345) (2017) 1376–1379.

[16] L. Meng, J. You, Y. Yang, Addressing the stability issue of perovskite solar cells for commercial applications, Nat. Commun. 9 (2018), 5265.

[17] A. Babayigit, A. Ethirajan, M. Muller, B. Conings, Toxicity of organometal halide perovskite solar cells, Nat. Mater. 15 (2016) 247–251.

[18] C. Eames, J.M. Frost, P.R.F. Barnes, B.C. O'Regan, A. Walsh, M. Saiful Islam, Ionic transport in hybrid lead iodide perovskite solar cells, Nat. Commun. 6 (2015), 7497.

[19] P.H. Joshi, L. Zhang, I.M. Hossain, H.A. Abbas, R. Kottokkaran, S.P. Nehra, M. Dhaka, M. Noack, V.L. Dalal, The physics of photon induced degradation of perovskite solar cells, AIP Adv. 6 (2016), 115114.

[20] K. Domanski, B. Roose, T. Matsui, M. Saliba, S.H. Turren-Cruz, J.P. Correa-Baena, C.R. Carmona, G. Richardson, J.M. Foster, F. De Angelis, J.M. Ball, A. Petrozza, N. Mine, M.K. Nazeeruddin, W. Tress, M. Grätzel, U. Steiner, A. Hagfeldt, A. Abate, Migration of cations induces reversible performance losses over day/night cycling in perovskite solar cells, Energy Environ. Sci. 10 (2017) 604.

[21] W. Nie, J.C. Blancon, A.J. Neukirch, K. Appavoo, H. Tsai, M. Chhowalla, M. A. Alam, M.Y. Sfeir, C. Katan, J. Even, S. Tretiak, J.J. Crochet, G. Gupta, A. D. Mohite, Light-activated photocurrent degradation and self-healing in perovskite solar cells, Nat. Commun. 7 (2016), 11574.

[22] J.A. Schwenzer, L. Rakocevic, R. Gehlhaar, T. Abzieher, S. Gharibzadeh, S. Moghadamzadeh, A. Quintilla, B.S. Richards, U. Lemmer, U.W. Paetzold, Temperature variation-induced performance decline of perovskite solar cells, ACS Appl. Mater. Interfaces 10 (2018) 16390–16399.

[23] M. Hirasawa, T. Ishihara, T. Goto, K. Uchida, N. Miura, Magnetoabsorption of the lowest exciton in perovskite-type compound(CH$_3$NH$_3$)PbI$_3$, Physica B 201 (1994) 427–430.