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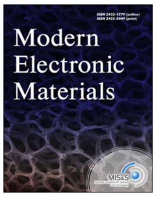

Current state and perspectives for organo-halide perovskite solar cells. Part 1. Crystal structures and thin film formation, morphology, processing, degradation, stability improvement by carbon nanotubes. A review☆

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ABSTRACT

The fundamental problems of the modern state of the studies of organic–inorganic organo-halide perovskites (OHP) as basis for high efficiency thin film solar cells are discussed. Perovskite varieties and background properties are introduced. The chronology of development of the studies in this direction has been presented – structural aspects of these OHP perovskites, from early 2D to recent 3D $MAPbI_3$ perovskites and important technological aspects of smooth thin film structure creation by various techniques, such as solvent engineering, spin- and dip - coating, vacuum deposition, cation exchange approach, nanoimprinting (particularly, a many-sided role of polymers). The most important theoretical problems such as electronic structure of lattice, impurity and defect states in pure and mixed perovskites, suppressed electron-hole recombination, extra-long lifetimes, and diffusion lengths are analyzed. Degradation effects associated with moisture and photo irradiation, as well as degradation of metallic electrodes to OHP solar cells have been considered. The application of carbon nanostructures: carbon nanotubes (CNT) and graphene as stable semitransparent charge collectors to OHP perovskites is demonstrated on the example of original results of authors.

1. Introduction

Global energy crisis and environment pollution become threatening factors for human being evolution. Addressing these problems is in the field of development of effective alternative renewable sources of energy. Undoubtedly, among a variety of such natural sources a leading place is occupied by solar radiation.

Unlike the traditional sources such as coal and fuel, the sun is a reliable steady and stable source of energy. The traditional solar cells on the basis of silicon and other combinations of inorganic semiconductors provide conversion up to 30%, but their wide application is restricted by high cost.

The photovoltaic devices (PD) converting solar energy into electric one are a base of many compositions and technologies of solar cell creation.

Therefore, development of new efficient technologies of PD is of great interest for industry.

A list of alternative and very promising PD technologies having low cost contains organic photovoltaics (OPV), solar cells with dyes (DSSCs) as absorbers and thin-film technologies.

The absorber efficiency is defined by a width of the interval of absorbing the wave lengths of solar radiation (350–950 nm) and a completeness of the conversion of incident light on charges.

The thin-film solar cells are significantly cheaper, as compared to highly crystalline silicon, owing to low cost of initial components and production process. At the same time, the production of classical cells based on thin-film Si and inorganic compound semiconductors requires vacuum and high temperature, which inevitably leads to higher cost. The organic photovoltaic cells are technological in production. However, owing to fundamental energy losses in the process of charge dissociation on bulk hetero-transitions they have less conversion than the silicon cells.

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2. Chronology of development of solar cells based on perovskite

The perovskites with the general formula ABX_3, analogs of natural mineral $CaTiO_3$, were discovered by Weber in 1987; their structure and properties were studied in detail by Mitzu et al. [1–5] when they created field transistors and light diodes. The total characteristics of the ABX_3 compounds were given by the Stoumpos group [6]. Semiconductor perovskite **(SP)** is a special class of the materials meeting all the requirements for solar radiation adsorbers, namely direct-zone with the high coefficient of absorption and charge mobility [5,7]. Perovskites are very technological for formation of corresponding layers through a solution on different substrates. The beginning of perovskite application is connected with solar cells on the basis of dyes. The first solar cell based on perovskite $CH_3NH_3PbBr_3$ with I^-/I_3^- electrolyte with conversion 2.19% was created by Miyasaka et al. in 2006 [8]. Afterwards, modifying mesoporous titanium oxide and electrolyte nature, the same group could get conversion 3.13% and 3.81% for perovskites $CH_3NH_3PbBr_3$ and $CH_3NH_3PbI_3$, respectively [9]. It was remarkable that for perovskite bromide the voltage of open circuit (V_{oc}) was about 1 V. However, the authors noted that owing to perovskite solving in acetonitrile the cells stopped to operate. Substitution of acetonitrile with a nonpolar solvent – ethylacetate [10] allowed conversion 6.2% (much higher than for dye No. 719 – 3.89%). However, in this case and for the same reason the cells lost their 80% efficiency for 10 min. It should be noted that because of the dimensional dependence of opto-electric characteristics the authors attributed the created cell architecture to a class of the cells sensibilized with quantum dots (QD) as such was, in this case, $CH_3NH_3PbI_3$. The use of QD (CdS, CdSe, PbS, PbSe, InP, InAs, Sb_2S_3) as absorbers instead of dyes was the most significant stage in solar cell development [9–15].

In spite of the good photovoltaic parameters the cells on the basis of quantum dots are instable. They have low V_{oc} and rapid recombination of charges, which impedes to achieve the high conversion efficiency.

The problem of perovskite solubility in liquid electrolyte was solved by Kim et al. [16] by electrolyte replacement with a hole-transport semiconductor spiro-OMeTAD (2,2′,7,7′ – tetrakis (N, N-di-p-methoxypheniamine) – 9,9' – spirobifluorene). The conversion was 9.7% with operability at the level of this conversion for approximately 500 h. By photoinduced absorption spectroscopy the authors found two processes – injection of holes from perovskite to spiro-OMeTAD and electrons to mesoporous TiO_2.

A little bit later but in the same year, Etgar et al. [17] demonstrated that the nano-particles of perovskite iodide can be simultaneously an absorber and a conductor of holes. For a cell without hole transporter with the use of titanium oxide nano-plates exposed in plane 001 the conversion was obtained 5.5% for standard power of solar simulator AM 1.5 1000 Wt/m^2 and 7.3% for lower intensity 100 Wt/m^2. In another work at the same time, using a thin-film technology, Lee [18] showed that mixed perovskite $CH_3NH_3PbI_2Cl$ has simultaneously the properties of a nice absorber and conductor of electrons. Using spiro-OMeTAD as a hole transporter and mesoporous Al_2O_3 (an insulator with the band gap 7–9 eV) instead of titanium oxide the authors obtained conversion 10.9% (8% with titanium oxide). The cells with such construction were called as mesosuperstructured ones. In a number of the key aspects of development of this direction an experimental fact should be noted. This fact was found by Snaith et al. [19] when they measured the diffusion lengths of electrons and holes for the planar configuration of cells (p–i–n structure) on the basis of perovskite iodide and chlorine-doped perovskites. These values are sufficiently balanced and averaged about 100 nm and over 1000 nm, respectively. Despite the fact that the reasons for such a behavior have not been revealed until now these results were used to select architecture of the cells with iodine and mixed perovskite. Namely, for $CH_3NH_3PbI_2$ a mesoporous configuration of the cell is acceptable and for $CH_3NH_3PbI_{3-x}Cl_x$ a planar one is quite acceptable. From the practical point of view the latter is more preferable owing to manufacturability. In a series of the subsequent works published in 2013–2015 almost everybody noted how it is important to make a highly qualitative film of perovskite with a maximal degree of crystallinity and covering of a corresponding substrate (mesoporous or dense metal oxides). Addressing those problems became a base for so rapid strengthening of the power conversion efficiency of the perovskite-based cells. Detailed consideration of this problem is mainly connected with a non-controlled development of the morphology in the process of perovskite film formation. The group Grätzel [20,21] realized a sequential deposition of the precursors of perovskite iodide, namely at first a film is formed from the PbI_2 solution on a mesoporous substrate and then it is dipped in the solution of methylammonium iodide. As a result of the proposed method, the cells with high reproducibility and conversion ~15% were obtained. Developing the ideas on optimization of conditions of perovskite film formation, Snaith et al. [22] realized a vacuum deposition of the precursors $CH_3NH_3PbI_{3-x}Cl_x$ in the planar configuration of the cell and achieved the conversion ~15.4%.

Taking into account that the vacuum deposition is a complicated technological process, Chen [23] proposed a similar technology [20] differed by the second stage: instead of dipping, the lead iodide film moves through vapors of methylammonium iodide. The kinetically favorable conditions of the precursor interaction lead to formation of a qualitative film of perovskite with an optimal coverage of the dense titanium oxide in the planar configuration of the cell on the basis of perovskite iodide. As a result, the best conversion efficiency exceeding 12% was obtained for this perovskite. A three-step technology [24] of producing a perovskite film deserves attention. This technology allows excluding a film of non-reacted PbI_2.

Great attention was paid by the researchers to selection and modification of materials with electron and hole transportation. Modification of dense titanium oxide in the planar configuration of cells with small amounts of graphene [25] and titanium diisopropoxide bis (acetilacetonate) [26] to decrease series resistance allowed for mixed perovskite the conversion efficiency 15.6% and 15.9%, respectively. Coordination of the energy levels of the hole-transport component (poly – triarylamine – PTAA) [27,28] and spiro – OMeTAD [29] and optimization of series resistance allowed strengthening the conversion efficiency from 16% to 19.3% [30].

The rapid growth of publications for recent years and conversion efficiency (Fig. 1) of the cells on the basis of perovskites as compared to alternative approaches is evidence of reasonable forecasts [31] of about the 25% conversion. There is every reason to hope that in the nearest time this value will be comparable with that of the cells on the basis of crystalline silicon.

The unusually fast steady growth of performance of perovskite photovoltaic cells is based on new exciting physics processes, which are found in 3-D perovskite semiconductors. Although many of them are not yet well understood, we need to outline here the most important and unusual features of perovskite electronic and optical properties, which have been found by different groups [32–34].

Impressive power conversion efficiency of solar cells based on hybrid lead halide perovskites reported in recent years still awaits a solid understanding of its microscopic origin. So photocarrier density and intrinsic Hall mobility, directly obtained in these materials in steady-state transport measurements, unambiguously demonstrate that both electron-hole recombination and charge trapping processes are suppressed. Electron-hole recombination coefficient explicitly measured in experiments ([35] on Hall Effect) (10^{-11}–10^{-1} $cm^3\ s^{-1}$) is on par with some of the lowest coefficients in high-purity single crystals of direct-band inorganic semiconductors. Such as GaAs. Steady-state carrier lifetimes (up to ~3 ms) and diffusion lengths