



## Prospects for the Use of Carbon-based Perovskite Solar Cells

Vladislav A. Kinev<sup>1</sup>, Pavel P. Gladyshev<sup>1\*</sup> and Medhat A. Ibrahim<sup>2</sup>

<sup>1</sup>Dubna State University, 19 University Str., Dubna, 141980, Moscow region, Russian Federation.

<sup>2</sup>Spectroscopy Department, National Research Center, 33 El-Bohouth Str., 12622 Dokki, Giza, Egypt.



**F**OR the first time, perovskite solar cells were demonstrated in 2009, and since then have been the subject of intense study. Due to the fact that perovskite has a band gap zone with direct transitions, it absorbs light more efficiently than silicon, and a thin layer is required to produce a solar cell, which can be obtained by precipitation from solution, which significantly reduces the cost of production of perovskite solar cells. Recently organic-inorganic hybrid lead-halide perovskite solar cells (PSCs) achieved a certified energy conversion efficiency of 23.7%. Among the various types of PSCs, carbon-based hole-conductor-free perovskite solar cells (CPSCs) were gradually recognized as the most promising for the commercialization with the advantages of low cost, high stability and easy fabrication. Here we review the latest developments in the field of printable carbon-based hole-conductor-free perovskite solar cells.

**Keywords:** Perovskite solar cells, Hole-conductor-free, Carbon materials.

### Introduction

Semiconductor photoelectric converters are the most efficient devices for converting solar radiation energy into electrical energy. The exceptional photovoltaic properties demonstrated for organic-inorganic hybrid lead-halide perovskites (for example,  $\text{CH}_3\text{NH}_3\text{PbX}_3$ , X = Cl, Br, I) attracted immense attention from scientists all over the world [1-6]. Intriguing optoelectronic characteristics include broad spectral absorption, low exciton binding energy, high charge carrier mobility and a significant diffusion length of charges [7-11]. Organic-inorganic hybrid lead-halide perovskite solar cells (PSCs) rapidly appeared on the leading edge of photovoltaic technologies with a certified power conversion rate of 23.7% [12].

A  $\text{TiO}_2$ / perovskite/ HTM/ Au device configuration is commonly used in typical PSC. Spiro-OMeTAD or PTAA (poly(triaryl)amine) are the most common choice for hole transport materials (HTM) [13-15]. However, the high cost

of spiro-OMeTAD or PTAA and their instability under the influence of atmospheric air becomes a serious problem for the development of PSCs [16-18]. Fortunately, perovskite material (such as  $\text{CH}_3\text{NH}_3\text{PbX}_3$ ) has a high mobility of charge carriers and can serve as the hole carrier itself, which makes it unnecessary to use additional material to transport them [19-23]. However, the absence of HTM layer causes a decrease in the efficiency of the PSCs, because the HTM not only transfers holes, but also blocks electrons, preventing the recombination of charges, which is a very important point.

HTM-free perovskite solar cells mainly include Au-based or carbon-based PSC [19,21,24-27]. However, Au is too expensive for mass industrial manufacture. Evaporating Au or Ag onto the top of the cell is a high energy-consumption process which needs high vacuum and high temperature, thereby limiting its commercial use [28-31].

To create simple and inexpensive photovoltaic device there were developed carbon-based PSCs not containing HTM [20,21,23,32-36]. Carbon

\*Corresponding author e-mail: [pglad@yandex.ru](mailto:pglad@yandex.ru)

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materials, especially graphite, carbon black and carbon nanotubes, have such characteristics as low cost, high electrical conductivity, accessibility, controlled porosity, chemical stability and environmental friendliness [37]. Taking these advantages, carbon is considered the most promising for electrode materials [22, 38]. In 2013, the Han group firstly reported about carbon-containing mesoscopic perovskite solar cells (m-CPSCs) without HTM [20]. Mesoscopic three-layer frame can be made by simple and cheap screen-printing technology, which offers a more positive perspective for commercial production [38]. In addition, they used  $(\text{HOOC}(\text{CH}_2)_4\text{NH}_3)_x(\text{CH}_3\text{NH}_3)_{1-x}\text{PbI}_3$  (hereinafter  $(5\text{-AVA})_x(\text{MA})_{1-x}\text{PbI}_3$ ) as a light absorber in the form of m-CPSCs and achieved a certified efficiency of 12.84% which was stable for more than 1000 hours without encapsulation in atmospheric air under the influence of light AM 1,5 G [21]. Recently, they manufactured a large-sized ( $10 \times 10 \text{ cm}^2$ ) printed mesoscopic perovskite solar module with an efficiency exceeding 10%. It is stable in local environmental conditions for 1 month and resistant to storage for more than one year [39]. Thus, the excellent characteristics of carbon-based m-CPSCs without the use of HTM make it one of the most promising solar cells for commercialization.

#### Device architecture and working principle

Carbon-based PSCs without HTM can be divided into two categories based on different types of carbon electrodes, such as a mesoscopic carbon electrode and a flat carbon electrode. As shown in Fig. 1a, typical HTM-free mesoscopic carbon-based PSCs (m-CPSCs) have a triple mesoscopic layer comprising  $\text{TiO}_2$ ,  $\text{ZrO}_2$  and carbon, acting as an electron transport layer, separation layer and hole collection layer, respectively. Triple layer is screen printed on FTO substrate layer by layer, followed by sintering. Then the perovskite precursor solution is infiltrated into the mesoscopic framework by drop-casting precursor solution from the carbon side. Perovskite crystals are formed after annealing. The schematic structure of a planar HTM-free carbon-based PSCs (p-CPSCs) consists of FTO/ $\text{TiO}_2$ /perovskite/carbon, as shown in Fig. 1b. Unlike m-CPSCs, p-CPSCs are manufactured in the same way as conventional PSCs using an Au electrode. Layers of m- $\text{TiO}_2$  and perovskite are deposited by spin coating on a thin planar layer of  $\text{TiO}_2$  deposited on FTO, and then the layer of carbon is deposited on the surface of the perovskite layer [23,35,40].

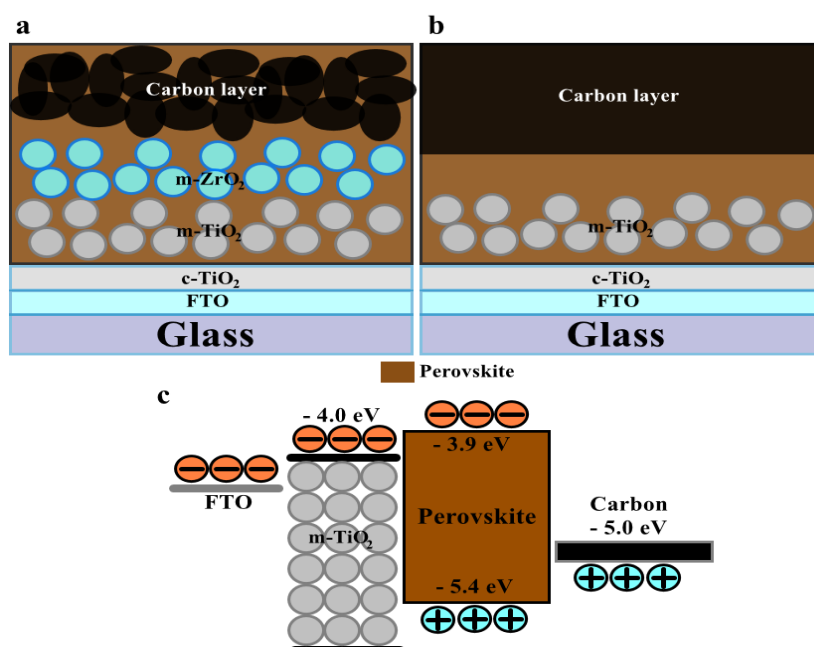


Fig.1. Schematic illustration of the structure of devices (a) m-CPSCs and (b) p-CPSCs. (c) Energy band diagram of CPSCs device.

The alignment of energy levels for three functional layers in the CPSCs device is presented in Fig. 1c. The conduction band edge (-3.9 eV) of perovskite MAPbI<sub>3</sub> is higher than the conduction band edge (-4.0 eV) of TiO<sub>2</sub>, and the edge of the valence band (-5.4 eV) is lower than the Fermi level (-5.0 eV) of carbon. Electrons and holes are generating in the conduction band and the valence band of MAPbI<sub>3</sub> after absorption of light radiation by the perovskite absorber. Then the photogenerated electrons move to the conduction band of TiO<sub>2</sub>, the holes are extracted by carbon. Spacer layer, such as m-ZrO<sub>2</sub>, is commonly used in m-PSCs without HTM to separate the TiO<sub>2</sub> and carbon layer. Due to the absence of the HTM layer, direct contact of the TiO<sub>2</sub> and the carbon layer can lead to a short circuit and then seriously affect the operation of the device. However, the separation layer is not needed for p-CPSCs without HTM, a thick layer of perovskite material on the surface of TiO<sub>2</sub> usually strongly separates TiO<sub>2</sub> and carbon.

#### Carbon-based HTM-free Perovskite solar modules

It is necessary to manufacture large-sized perovskite solar modules (PSM) for commercialization of PSCs. Recently, Hu et al. [39] have successfully achieved new results, when they created PSM systems without HTM with sizes up

to 100 cm<sup>2</sup> using cost-effective screen-printing technology (Fig. 2). Carbon-based perovskite solar modules (CPSM) (10x10 cm<sup>2</sup>) are consisted of 10 series-connected cells showing an efficiency of 10.4% in the active area of 49 cm<sup>2</sup> (Fig. 3). PSM showed good stability without encapsulation during continuous illumination for 1000 hours in ambient conditions with a temperature of 25 °C and humidity (RH) of 54%. The surface temperature of the device reached 50 °C and were stabilized throughout the test under continuous illumination. They also tested the external stability of encapsulated devices for 1 month in a local environment with an average temperature of around 30 °C and an RH of 80% in Wuhan, China, and no deteriorations was observed. In addition, they made a fully printable 7 m<sup>2</sup> perovskite solar panel, demonstrating good reproducibility of screen-printing technology in the manufacture of high-performance PSM. This paved the way for the implementation of an efficient and stable large area PSM for industrial deployment. At the same time, the Subodh group also produced a 70 cm<sup>2</sup> PSM on the basis of the exact same structure, which shows stability in the environment for more than 2000 hours with a decrease in efficiency less than 5% [41]. The main achievements of the study of PSCs without HTM are represented in Table 1.

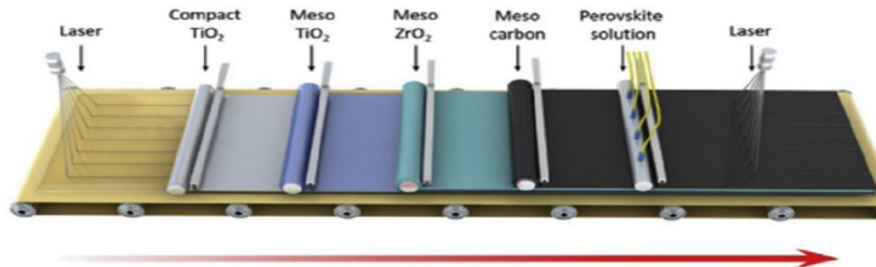


Fig. 2. Schematic illustration of the proposed production line of PSM.[39].

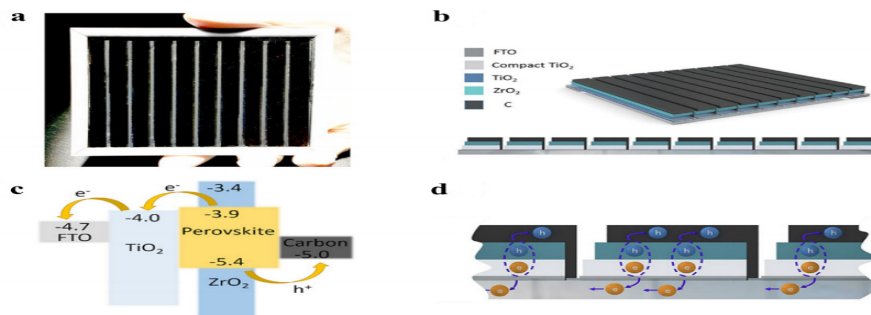


Fig. 3. (a) Image of a monolithic printable PSM with 10 subcells. (b) The monolithic interconnection scheme of the module. [39]

**TABLE 1. Main devices of CPSC type without HTM and indications of their effectiveness.**

Device structure	PCE (%)	Ref.
FTO/(TiO <sub>2</sub> /ZrO <sub>2</sub> /carbon)/MAPbI <sub>3</sub>	6,64	[20]
FTO/(TiO <sub>2</sub> /ZrO <sub>2</sub> /carbon)/MAPbI <sub>3</sub>	12,84	[21]
FTO/(TiO <sub>2</sub> /ZrO <sub>2</sub> /carbon)/MAPbI <sub>3</sub>	13,89	[44]
FTO/(TiO <sub>2</sub> /ZrO <sub>2</sub> /carbon)/MAPbI <sub>3</sub>	14,50	[43]
FTO/(TiO <sub>2</sub> /ZrO <sub>2</sub> /carbon)/MAPbI <sub>3</sub>	15,60	[42]
FTO/TiO <sub>2</sub> /MAPbI <sub>3</sub> /carbon	8,31	[36]
FTO/TiO <sub>2</sub> /MAPbI <sub>3</sub> /carbon	9,08	[30]
FTO/TiO <sub>2</sub> /MAPbI <sub>3</sub> /carbon	13,53	[35]
FTO/TiO <sub>2</sub> /MAPbI <sub>3</sub> /carbon	14,38	[45]
FTO/TiO <sub>2</sub> /MAPbI <sub>3</sub> /CNTs	6,29	[48]
FTO/TiO <sub>2</sub> /MAPbI <sub>3</sub> /MCWNTs	12,67	[49]
FTO/TiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> /MAPbI <sub>3</sub> /MCWNTs	15,23	[52]
FTO/(ZnO/TiO <sub>2</sub> /ZrO <sub>2</sub> /carbon)/MAPbI <sub>3</sub>	8,24	[50]
FTO/TiO <sub>2</sub> /SiO <sub>2</sub> /MAPbI <sub>3</sub> /carbon	11,90	[51]
FTO/TiO <sub>2</sub> /CsPbBr <sub>3</sub> /carbon	6,70	[47]
FTO/TiO <sub>2</sub> /(FA) <sub>x</sub> (MA) <sub>1-x</sub> PbI <sub>3</sub> /carbon	13,03	[46]

#### *Molecular modeling approaches*

Molecular modeling with different level of theories is applying the basis of physics to understand chemical structures and materials functionality [53].

Molecular modeling offers tools for investigating chemical structure in which experimental setup is limited and/or unavailable [54-55]. It's now an effective tool to elucidate the functionality of emerging and new materials based on their electronic properties [56-60]. The structural properties, the efficiency of absorption and reflection of the solar cell made of perovskites could be investigated with molecular modeling at density functional theory DFT level of theory [61-63]. It is stated that, combining both DFT and finite difference time domain (FDTD) method could an effective tool of computation to assess the different properties of solar cell made of perovskites [64]. It is also stated that, relativistic GW approximation has been demonstrated to provide electronic structure accurately with extremely high computational cost [65-68]. Attempts were carried out by many researchers to predict the properties of newly designed perovskites with accurate at a low computational cost [69]. An exchange-correlation functional

based on DFT is utilized to predict the band gap in organic-inorganic metal halide perovskites [70].

It could be concluded in this section that DFT as well as modified DFT level of theories are dedicated now to investigate and/or innovate new features for perovskite solar cells. This findings is in good agreement of the previous findings [71-73].

#### **Conclusion and outlook**

In this paper we focused on recent advances of low-cost carbon-based hole-conductor-free perovskite solar cells in terms of perovskite solar cell modifications and large surface perovskite solar modules. Carbon-based PSCs without HTM demonstrate high stability during continuous illumination in environmental conditions, which makes them one of the most promising solar cells for commercialization. However, the current efficiency for HTM-free CPSCs is still lower than that of conventional PSCs based on HTM. Therefore, improving the efficiency of devices is a major priority.

The mechanism of excellent stability of HTM-free CPSCs has not been fully studied. Further work should focus on studying of the relation between stability of the device properties and the peculiarities of its internal architecture, as well as

on the establishment of the aging mechanism of various PSCs components.

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## أفاق استخدام خلايا بيروفسكايت الشمسية القائمة على الكربون

فلاديسلاف كينيف<sup>1</sup>، بافل جلاشيف<sup>1</sup> و مدحت ابراهيم<sup>2</sup>

<sup>1</sup>جامعه دوبنا- دوبنا- روسيا الاتحادية.

<sup>2</sup> قسم الطيف- المركز القومي للبحوث - 33 شارع البحوث - 12622 الدقى- الجيزة- مصر.

عام 2009 تم لأول مره استخدام الخلايا الشمسية التي تعتمد علي مواد البيروفسكايت في تكوينها. ومنذ ذلك الحين أصبحت مواد البيروفسكايت من المواد المهمة التي تدخل في تركيب الخلايا الشمسية نظرا لكفاءة امتصاص الضوء التي تتمتع بها. وزادت اهمية هذا النوع من المواد في الخلايا الشمسية بعد استخدام طريقة الترسيب الكيميائي ذات البعد الاقتصادي في التحضير. كما تم مؤخرا تحضير مزيج مهجن من بيروفسكايت يحتوي علي مواد عضوية وغير عضوية مثل

Organic-inorganic hybrid lead-halide perovskite solar cells (PSCs)

استخدمت كخلايا شمسية بكفاءة بلغت حوالي 23.7%. والجدير بالذكر ان هناك محاولات تطوير مستمرة في هذا المجال لتقليل التكلفة وذلك باستحداث خلايا شمسية من النوع

Carbon-based hole-conductor-free perovskite solar cells (CPSCs)

والغرض هو الحصول علي درجة ثبات اعلي وتكلفة اقل في مجال استخدام مواد البيروفسكايت في تحضير الخلايا الشمسية.