DEPENDENCE OF THE MORPHOLOGY OF METHYLAMMONIUM LEAD TRIHALIDE ON THE PROCESSING CONDITIONS IN FULLY PRINTABLE SOLAR CELLS

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Introduction

Organic-inorganic lead halide compounds CH$_3$NH$_3$PbX$_3$ (X = Br, I) with perovskite structure are effectively used as visible-light sensitizers in low-cost thin-film solar cells. A mesoporous film of TiO$_2$ is traditionally used as a photoanode for electrons injected from the photoexcited compound [1, 2]. A hole-conducting layer may be embodied in an organic electrolyte solution [1] and polymeric materials [3] but one of the most simple and stable hole transporting layer is composed of ZrO$_2$ [4]. Both mesoporous oxide layers form a scaffold infiltrated with methylammonium lead iodide (see Fig. 1).

Methylammonium lead iodide is synthesized from the solutions of precursors PbI$_2$ and CH$_3$NH$_3$I$_3$ (MAI) according to the reaction:

$$\text{CH}_3\text{NH}_3\text{I} + \text{PbI}_2 \rightarrow \text{CH}_3\text{NH}_3\text{PbI}_3.$$

One- and two-step ways of the synthesis are possible. At the one-step method, both precursors are dissolved in a suitable solvent, deposited
on the TiO₂ or ZrO₂ layer and heated. Visually completion of synthesis is manifested in changing color of the layers from yellow to black. According to the two-step way, firstly, the solution of PbI₂ is deposited on a mesoporous oxide layers and dried and, after that, the sample is dipped into the MAI solution, heated and dried. An excess amount of MAI is removed by washing in a solvent. However, perovskite crystallization from a solution produces has large morphological variations. It was demonstrated that the highest photocurrents are attainable only with the highest perovskite surface coverages [5]. The work is devoted to dependence of methylammonium lead trihalide morphology on synthesis and processing conditions.

**Experimental**

**Inkjet printing of methylammonium lead trihalide**

Mesoporous layers of TiO₂ and ZrO₂ were ink-jet printed with Dimatix 2850 printer. Ink-jet printing of methylammonium lead iodide is a new method, there are a few works devoted to this process [6]. In view of [6], the one-step way was selected for elaborating the printing mode of methylammonium lead trihalide, as simpliest. In printing, stability of drop formation depends on a shape of a voltage pulse applied to a jet of a printing head and its maximum value. Jetting frequency, drop spacing and shape of a voltage pulse correlate to ink viscosity and surface tension. The ink (precursors solved in polar organic solvent dimethylformamide (DMF)) was placed into the printing cartridge made of polypropylene resistant to polar solvents.

Ink composition 1:0.5 mmol CH₃NH₃I, 0.5 mmol PbI₂, and DMF 1 ml. Ink surface tension was 34.66 mN/m, which is similar to the recommended value of 30 mN/m while the value of viscosity was 1.98 cP, significantly lower than the optimal value of 30 cP. Special electric voltage form on printer nozzles was selected to get a stable regime of printing.

Ink-jet printed samples of methylammonium lead trihalide included 1, 2 and 3 layers on a glass substrate and TiO₂ layer. Each perovskite layer on the sample had dimensions of 20x20 mm and was formed by 0.81 µL of the ink (251 µg of perovskite). After vacuum drying, the samples were thermally treated at temperature of 100°C for 30 min. Fig. 2 presents photographs illustrating the structure of perovskite crystals CH₃NH₃PbI₃
obtained by means of electron microscope Hirox. In Fig. 3, UV and visual transmittance spectra of perovskite samples having 1, 2 and 3 printed layers are shown. As known [7, 8], a solvent influences on the synthetic reaction of perovskite. In the case of DMF, fast solvent evaporation can result in crystallization of the precursors, which form needle crystals having a diameter of 2-3 µm and length of 100 µm. Added to this is the fact that complex compounds (Lewis adduct) PbI₂·DMF and CH₃NH₃I·DMF also can form the similar structures. The formed needle crystals are distributed over the surface of the samples in a uniform manner which results in low light absorption. The fact that the crystal formation seems to be associated with printing is confirmed by absorption spectra shown in Fig. 3. The spectra in Fig. 3 were measured by means of Thermo Scientific™ GENESYS™ 10. It was shown that multiplying printed layers does not result in proportional increase in light absorption.

**Fig. 2.** Photographs of the printed layer of methylammonium lead trihalide obtained by optical microscope Hirox: (a) 1 layer on a glass substrate; (b) 1 layer on a glass substrate coated with TiO₂; (c) 2 layers on a combined glass/ titanium oxide substrate.

In order to optimize the shape of obtained crystals, molar ratio of precursors was varied. Specifically, ink composition 2 was the next: 0.6 mmol CH₃NH₃I, 0.4 mmol PbI₂, and DMF 1 ml. No changes in printing and thermal treatment were made. Photographs of the printed layer are presented in Fig. 4. As a result of changing molar ratio of precursors, formation of needle crystals was blocked but an amount of printed ink was
insufficient that impeded formation of a uniform layer having good light absorption.

**Fig. 3.** Absorption spectra of layers of methylammonium lead trihalide printed on a glass substrate.

![Absorption spectra](image)

**Fig. 4.** Photographs of the printed layer of methylammonium lead trihalide obtained by optical microscope Hirox at different magnification. (a) 2 layers on a titanium oxide substrate; (b) 2 layers on a zirconium oxide substrate.

![Photographs](image)
Fig. 5. Absorption spectra of methylammonium lead trihalide layers printed on a glass substrate having different precursor ratios in DMF solution.

**Characterization of obtained spectral characteristics in dependence on synthesis conditions**

To examine a dependence on synthesis conditions more closely, samples of perovskite layers were coated onto substrates by drop-casting from precursor solutions and synthesized at different conditions. Absorption spectra in UV and visible regions were measured. Table 1 provides detailed description of obtained samples while absorption spectra are presented in Fig. 6. Perovskite layer morphology was studied by optical microscope Hirox (see Fig. 7).

<table>
<thead>
<tr>
<th>No</th>
<th>Synthesis type</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>One-step</td>
<td>CH₃NH₃I: PbI₂ 1.5:1 in DMF</td>
</tr>
<tr>
<td>2</td>
<td>One-step</td>
<td>CH₃NH₃I: PbI₂ 1:1 in γ-butyrolacton</td>
</tr>
<tr>
<td>3</td>
<td>One-step</td>
<td>CH₃NH₃I: PbI₂ 3:1 in DMF</td>
</tr>
<tr>
<td>4</td>
<td>Two-step</td>
<td>1.1 mmol of PbI₂ solved in 1 mL of DMF; a substrate coated with 20 µL; drying at 40°C for 3 min. Solution of CH₃NH₃I in isopropanol 10mg/mL. Dipping the substrate coated with PbI₂ in 0.5 mL of CH₃NH₃I solution for 15 min. After change in the color of the PbI₂ layer, drying and rinsing in isopropanol. Heating at 70 °C for 30 min.</td>
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Fig. 6. Absorption spectra of samples on (a) a glass substrate and (b) a glass substrate coated with TiO$_2$.

Comparing the obtained absorption spectra, one can see the increase in absorption of both samples 3 and 4 made on the bare glass substrate and substrate coated with TiO$_2$.
Fig. 7. Photograph of methylammonium lead trihalide layer (optical microscope Hirox) (a) Sample 1; (b) Sample 2; (c) Sample 3; (d) Sample 4; Left photographs relate to the samples on the bare glass substrate; right photographs to the glass substrates coated with TiO$_2$.

Samples 3 and 4 in Fig. 7 demonstrate significantly smaller crystal dimensions and, as a result, improved covering power. We await that the
proposed conditions of perovskite synthesis can improve characteristics of perovskite-based solar cells due to increase in light absorption. Dependence of photogeneration on synthesis condition was studied by measuring luminescence spectra presented in Fig. 8. Luminescence spectra characterize efficiency of photoelectron generation defining an achievable photocurrent.

![Luminescence spectra of samples 1 to 4 of Table 1. Wavelength of excitation is 355 nm.](image)

**Fig. 8.** Luminescence spectra of samples 1 to 4 of Table 1. Wavelength of excitation is 355 nm.

It is known in the art that maximum absorption in the region of 770-790 nm (1.55-4.6 eV) corresponds to methylammonium lead iodide [9, 10]. Luminescence spectrum of PbI$_2$ includes a narrow line at 495 nm and a broad band at 510–530 nm [11, 12]. Fig. 8 indicates presence of unreacted lead iodide in the samples 1–3. Contrary to this, sample 4 includes a desirable compound synthesized when the precursors are almost completely reacted to each other. The two-step synthesis method proved to be more effective in the experimental conditions, and it needs for the further development of ink-jet printing process.

**Conclusion**

Ink-jet printing of methylammonium lead iodide (perovskite) is a new method. A few publications are devoted to this method, and there is a little experience in the field. The obtained results show a promising potential of ink-jet printing of perovskite precursors solved in an organic solvent and its synthesis on a ZrO$_2$ printed mesoporous layer. The
chemical composition of obtained layers depends on both precursor ratio and a synthesis procedure which define spectra of absorption and luminescence and, finally, electric characteristics including efficiency of the solar cell based on this photosensitive compound.

**Acknowledgements**

The authors thank Dr. Lev Naglii for the luminescence spectra.

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