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**SECOND INTERNATIONAL CONFERENCE
ON ELECTRON MICROSCOPY OF
NANOSTRUCTURES**

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Improving the contact surface between TiO₂ nanotubes and MAPbBr₃ to make perovskite solar cells

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The organo-inorganic perovskites are extraordinary materials that have recently revolutionized the field of photovoltaics due to their low-cost fabrication and high optical absorption. In a short period, they reached great efficiency. Many parameters which affect the quality of perovskite films can be optimized, so the efficiency of these devices can be further improved [1]. In perovskite solar cells, the perovskite layer is an active layer that absorbs the visible part of the spectrum, resulting in the formation of the electron-hole pair. To decrease the recombination of charge carriers, the construction of solar cells requires the existence of two additional layers in order to separate the holes and electrons. TiO₂ could be used as an electron transport layer because its conduction band (CB) lies under the CB of perovskite [2]. In that way, electrons diffuse from CB of perovskite to CB of TiO₂. For these experiments, TiO₂ nanotubular structure provides a one-dimensional transmission channel for the charge carriers, which resulting in faster carrier transport. Perovskite methylammonium lead bromide (MAPbBr₃) was coupled with TiO₂ nanotube arrays which were synthesized by anodization of Ti foil and annealed at 450 °C [3]. The most used methods for deposition of perovskite materials on mesoporous and planar TiO₂ are: one-step deposition, two-step sequential deposition, and vapor-assisted solution processing. Disadvantage of these methods is a small contact area between TiO₂ and perovskite [4,5]. The aim of this research was to increase the contact surface of the perovskite and TiO₂ nanotubes by filling the nanotubes with the perovskite material in order to improve electron transport. Due to that, two different methods were used for deposition of MAPbBr₃ crystals onto TiO₂ nanotubes: high vacuum assisted with nitrogen gas and application of the supercritical CO₂ as a cosolvent. The procedure of deposition of perovskite in a high vacuum system included degassing of the sample under a high vacuum for 3 h at 200 °C, cooling down the sample, and putting a solution of MAPbBr₃ in dimethylformamide (DMF) onto the sample, and then treating with inert gas (N₂), which enabled the filling of the nanotubes with perovskite material to some extent [6]. Deposition of solution perovskite on TiO₂ nanotubes assisted by supercritical carbon dioxide was done at 200 bar and 35 °C for 1 h. The supercritical fluid, CO₂ had a role of a cosolvent which would help the filling nanotubes with perovskite material. XRD analysis of synthesized perovskite confirms coincidence with literature data [6]. Morphological characterization of samples after deposition of perovskite was carried out by FESEM. It was observed that the filling of nanotubes is better when deposition of perovskite was assisted by supercritical CO₂. The measurement of the *I-V* characteristic under visible light shows that the value of current for this sample is also higher, so it could be concluded that a better contact between perovskite and TiO₂ nanotubes was achieved in this case. Perovskite photodiodes that were made in this study will be the basis for future solar cell construction.

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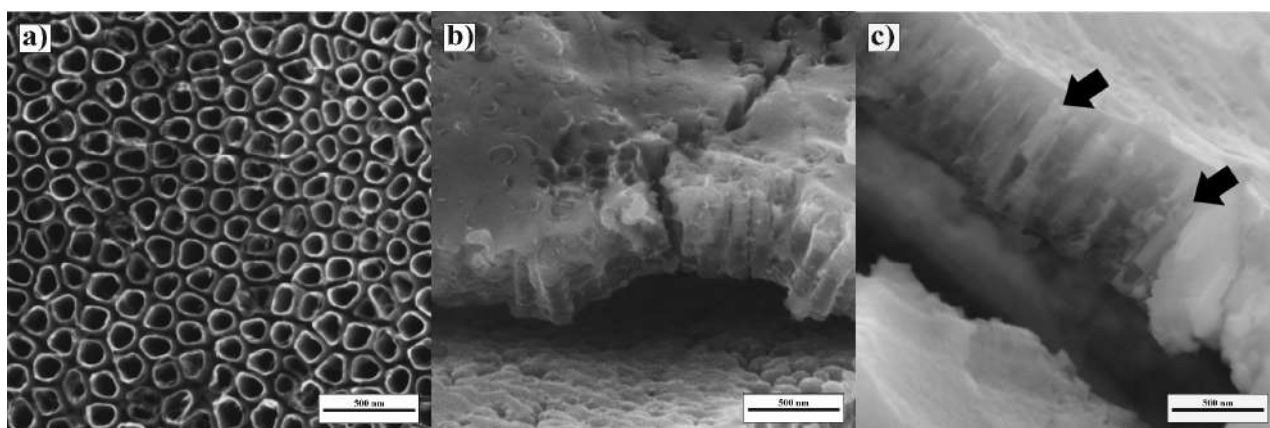


Figure 1. FESEM micrographs of a) pristine TiO₂ nanotube arrays, and TiO₂ nanotube arrays with MAPbBr₃ perovskite deposited b) in a high vacuum and inert gas [6] and c) assisted by supercritical CO₂ (the black arrow shows that the TiO₂ nanotubes are more filled with perovskite compared to the sample under b).

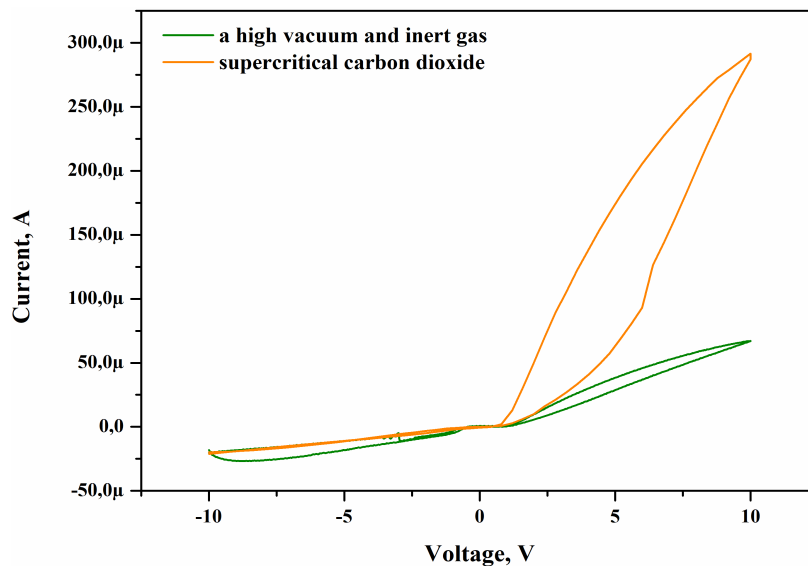


Figure 2. *I-V* characteristics of TiO₂ nanotubes-MAPbBr₃ perovskite photodiodes after preconditioning (poling at 10 V for 30 s) with external bias voltage under visible light. Hysteresis curves were obtained for both samples, but the value of current was higher for the sample which was done with supercritical CO₂. It supposes that one of the reasons is a larger contact surface between TiO₂ nanotubes and MAPbBr₃ perovskite.