

# Carbon Nanotube Electrodes for Semitransparent Perovskite Light-Emitting Electrochemical Cells

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**Abstract**—Multiwall carbon nanotubes can be used for development of semitransparent light-emitting electrochemical cells. Due to its chemical inertness, they can withstand highly corrosive materials like halide perovskites, which are the most promising material for fabrication of next generation optoelectronic devices. Here we investigate how perovskite-based light-emitting electrochemical cell can be fabricated only with carbon nanotubes as anode and cathode. We show that for the fabrication drop-casting technique should be used instead of conventional spin-coating method. High roughness of the multiwall carbon nanotubes can be overcome with drop casting method of material deposition that allows fabrication of thick films. Light-emitting electrochemical cells demonstrate relatively low maximum luminance of 50 cd/m<sup>2</sup> and we demonstrate the issue behind it.

**Keywords:** perovskite light-emitting electrochemical cells, MWCNT, ion migration

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## INTRODUCTION

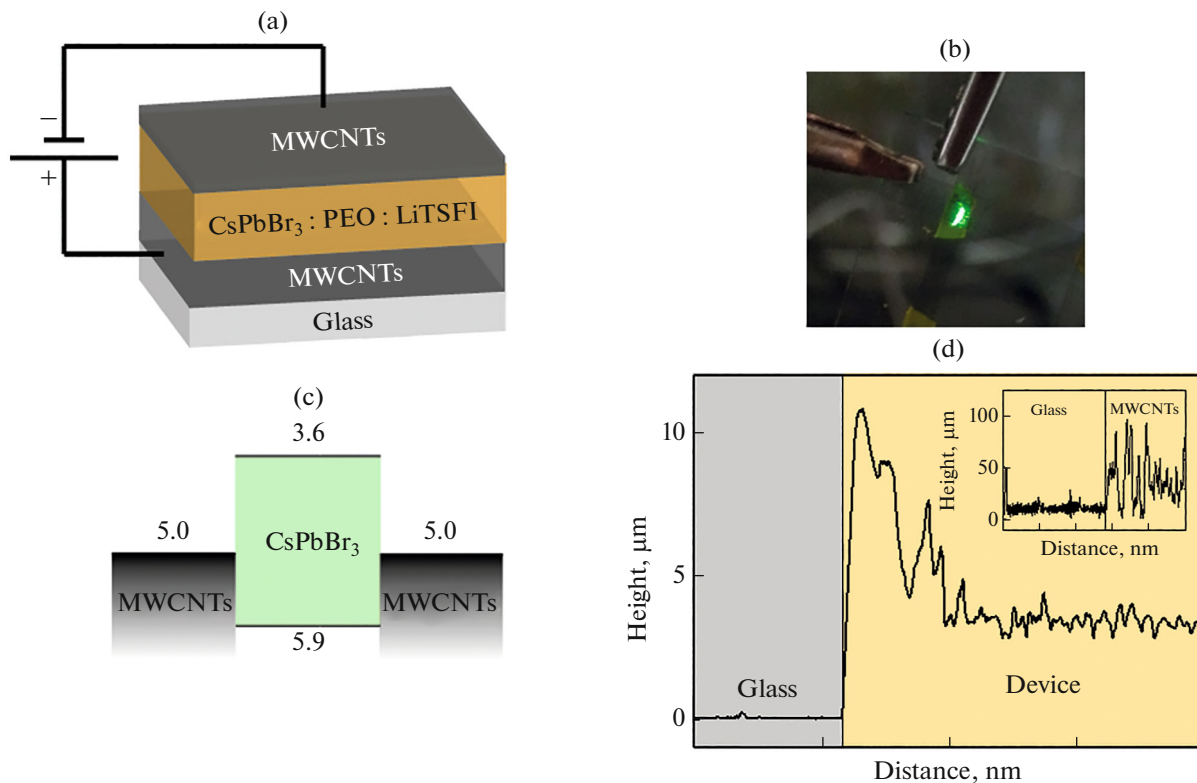
Light-emitting electrochemical cell (LEC) is the nearest and most perspective substitution of an organic light-emitting diode (OLED) [1, 2]. LEC has several advantages over OLED that make it promising for the development. The first advantage is simple device design, usually LEC has only one emissive layer or combination of emissive layer and one transport layer. The second advantage is absence of need for rigorous device encapsulation, LECs do not have air sensitive electrodes like barium, which needed due to its low work function. The third is independence on work function of electrodes due to formation of pin structure by mobile ions inside the emissive layer. These advantages arise from complex composition of emissive layer [1]. Emissive layer consists of solid polymer electrolyte (SPE), lithium salt and emissive material. Usually polyethylene oxide (PEO) serves as SPE [1, 3]. Lithium salt is the most important part of the mixture, it gives mobile ions that moves toward the interfaces of the emissive layer and electrodes under applied electrical bias. Emissive material can be chosen from the large variety of the materials, e.g., small molecules, quantum dots, complexes of transition metals, perovskite, etc. [1, 4–6].

Halide perovskite is one of the most promising materials for the development of the next generation optoelectronic devices like solar cells and light emitting devices [7, 8]. Nowadays, halide perovskites allow achievement of high efficiency of solar cell (~23%)

and LED (~20%) [9, 10]. But halide perovskite possesses one crucial property for the development of stable devices, which is ion migration [11]. Ions of halogen have low activation energy and demonstrate considerable movement even at room temperature. During the operation of the perovskite-based device halogen ions can accumulate at one interface and even penetrate the next layer, which is an electrode immediately reacting with metal and corroding it. For the inhibition of this process one can use additional layers so called diffusion barrier like lithium fluoride, which also improves the work function of the metal electrode [12].

The problem of the electrode corrosion can be also solved with the use of chemically inert materials like carbon nanotubes (CNT). CNTs are the most perspective material for the replacement of the typical electrodes in the optoelectronic devices: indium tin oxide (ITO) and metal electrode. CNTs can be synthesized by various methods and have different properties [13]. Multi-walled CNTs (MWCNTs) are the cheapest ones and found its application in various applications from electrical contacts to artificial muscles [14]. Although MWCNTs have poorer electrical parameters than single wall CNTs, which are superior and expensive ones [15].

In the present work we demonstrate how perovskite LEC (PeLEC) can be fabricated by simple drop-casting method with use of MWCNTs as electrodes.



**Fig. 1.** Device design. (a) Layer architecture of the device, (b) photograph of the device under applied bias demonstrating electroluminescence, (c) band diagram of the device, (d) thickness of the device, inset shows the thickness of MWCNT layer deposited on glass substrate.

## EXPERIMENTAL

A  $\text{CsPbBr}_3$  solution was prepared by dissolving lead bromide ( $\text{PbBr}_2$ , 99.99% Lankhit) and cesium bromide ( $\text{CsBr}$ , 99.9%, Lankhit) with a molarity of 0.2 in 1 mL of anhydrous DMSO solution. A polyethylene oxide (PEO) solution was prepared separately by dissolving 20 mg PEO ( $M_w = 1\,000\,000$  g/mol) in 1 mL DMSO, then the solution was stirred overnight at  $60^\circ\text{C}$  at 300 rpm to obtain homogeneous solution. The perovskite-polymer solution  $\text{CsPbBr}_3 : \text{PEO}$  (1 : 0.2 by weight) was prepared by mixing required masses of PEO and  $\text{CsPbBr}_3$  solutions. Finally, in the perovskite-polymer solution was added required amount of LiTFSI solution in DMSO (10 mg/mL). The resulting solution was stirred for 1 h at 300 rpm.

MWCNTs were used without any purifications. The stripes of MWCNTs were deposited on patterned ITO substrate and densificated with di-isopropyl ether. A drop of prepared solution was deposited on the top of the MWCNT layer and annealed at  $60^\circ\text{C}$  in vacuum for 1 min. Another MWCNT layer was deposited on the top of the perovskite material to form the pixel and it was also densificated with di-isopropyl ether.

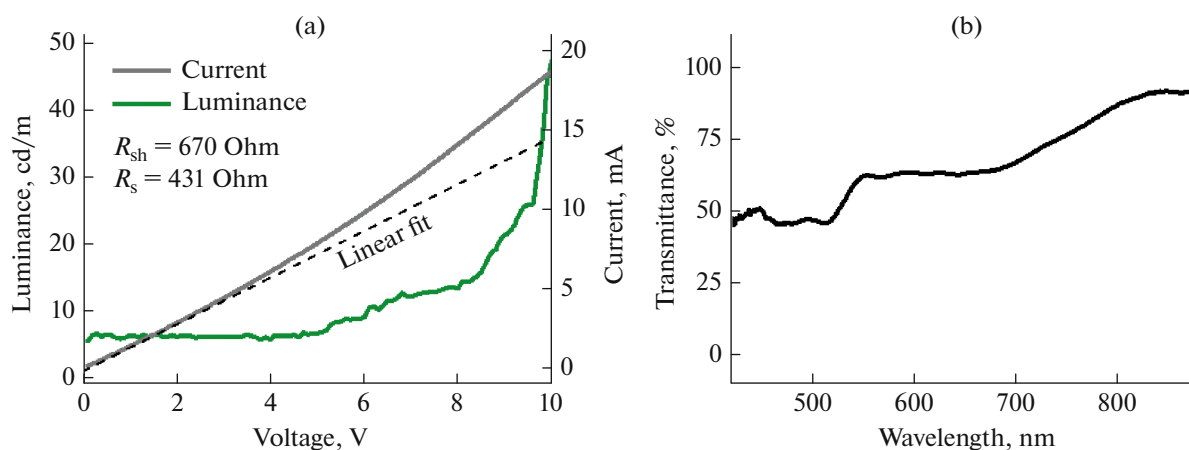
Measurement of IV curves was conducted with source-meter unit Keithley 2400 and luminance was

measured with spectroradiometer CAS-120 (Instrument systems).

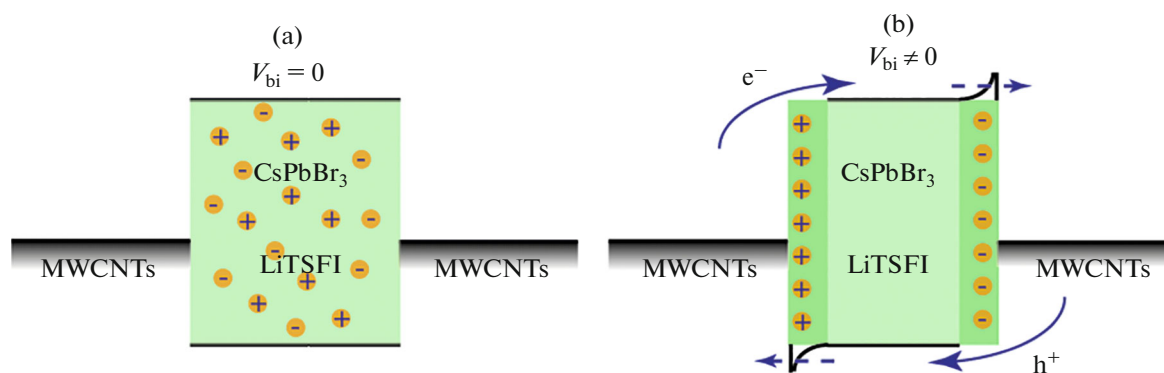
## RESULTS AND DISCUSSION

Figure 1 shows a design of the device and photograph of fabricated PeLEC with MWCNT as top and bottom electrode. MWCNTs under applied electrical voltage. The device was fabricated with MWCNT deposited onto glass substrate, MWCNTs have high roughness ( $>50$  nm) that makes conventional methods of deposition like spin-coating or doctorblading inapplicable to use for fabrication of these type of PeLECs. The thickness of the film, which can be obtained via spincoating method of this composition is usually around 120 nm. As a result, MWCNTs covered with a perovskite-polymer film deposited by spincoating will have high roughness that will lead to formation of a contact between top and bottom MWCNT layers, which will result in the absence of any electroluminescence. To solve this issue, we used a drop-casting method for synthesis of the perovskite film.

In this case a small drop of a perovskite solution (approx.  $5\ \mu\text{L}$ ) poured on top of the MWCNT layer and dried until the complete formation of perovskite. Drop-casting technique allows synthesis of thick films. In our case we obtain around  $2\ \mu\text{m}$  thick film



**Fig. 2.** (a) LIV dependence of the PeLEC with MWCNT electrodes. (b) Transparency of the assembled device.



**Fig. 3.** Evolution of the device band diagram: (a) initial device, (b) device under the bias.

(Fig. 1d). Then top layer of MWCNTs is deposited on top of the perovskite and intersection of top and bottom MWCNTs forms the pixel. Despite the high thickness of the perovskite film device still demonstrates low series resistance ( $\approx 400$  Ohm). Even at this high thickness of perovskite layer device demonstrates transparency around 50% (Fig. 2b).

Figure 2 shows measured current-voltage (IV) and current-luminance (LIV) characteristics of the device. The device does not demonstrate high brightness, the luminance of the device only reaches  $50 \text{ cd/m}^2$  at 10 V. Also, the IV curves don't demonstrate significant diode-like behavior (Fig. 2a). It means that device architecture does not provide charge carrier separation. As a result, electrons and holes injected from the MWCNTs into perovskite layer can freely pass the perovskite towards the opposite electrode. Injected charge carriers do not recombine in the perovskite layer leading to the low luminance.

Although the ionic migration of LiTFSI under applied bias should result in formation of doped regions (by  $\text{Li}^+$  and  $\text{Cs}^+$  or  $\text{Br}^-$  and  $\text{TFSI}^-$ ) near the MWCNT electrodes with following formation of  $p-i-n$

structure (Fig. 3). The formation of  $p-i-n$  structure usually results in enhancement of charge separation and enhancement of overall device performance [16]. But in our case, it seems that only  $p-i-n$  structure formed by migrating ions is insufficient to obtain considerable charge separation, which leads to resistor like IV curve and low shunt resistance ( $\approx 400$  Ohm) (Fig. 2a).

## CONCLUSIONS

Perovskite based light-emitting electrochemical cells can use MWCNTs as both electrodes. In this case, the device demonstrates luminance of  $50 \text{ cd/m}^2$ . Since in this case electrodes are identical it results in almost ohmic-like IV curve. Ohmic behavior of the IV curve originates from insufficient of charge separation provided by  $p-i-n$  structure formation inside the perovskite-polymer layer.  $p-i-n$  structure formed only by ions of LiTFSI and  $\text{CsPbBr}_3$  is not enough to obtain adequate charge separation inside the device that leads to propagation of charge carriers from one electrode to another without any limitations.

## FUNDING

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## CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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