Multi wall carbon nanotubes as a top electrode for perovskite light-emitting electrochemical cells

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Abstract. Carbon nanotubes are promising materials for use as flexible and transparent electrodes for a wide variety of optoelectronic devices like solar cells and light-emitting diodes. Moreover, the chemical inertness of carbon nanotubes matches with the operation of light-emitting electrochemical cells where ion migration is a main working principle especially based on halide perovskite, in which ions corrode metal electrodes. Here we demonstrate how the removal of synthesis residuals via synthesis enables the use of multiwall carbon nanotubes as a transparent electrode.

1. Introduction

Light-emitting electrochemical cells (LECs) are promising for the development of the next generation light-emitting devices owing to their numerous advantages like the use of air-stable electrodes, simple device design, scalable and cost-efficient processing, formation of p-i-n structure inside the photoactive layer [1–4]. Usually, LECs utilize simple single-layer device architecture, where one photoactive layer is sandwiched between transparent conductive oxide and metal electrodes. The photoactive layer consists of a mixture of solid polymer electrolyte (e.g., polyethylene oxide), lithium salt that is responsible for p-i-n structure formation inside the photoactive layer and luminescent material like ionic transition metal complexes, quantum dots, conjugated polymers, and halide perovskites [5–7].

Halide perovskites with the formula ABX³, where A is usually an ion of methylammonium (MA⁺), formamidinium (FA⁺) or cesium (Cs⁺), B is an ion of lead (Pb²⁺), and X is a halogen ion of iodine (I), bromine (Br⁻) or chlorine (Cl⁻) are a family of promising materials for realization of next generation of different optoelectronic devices like solar cells, light-emitting diodes due to its magnificent properties like the ease of processability, a wide variety of deposition methods, narrow luminescence line, compatibility with different materials [8]. LECs based on halide perovskites have already demonstrated...
high luminances and quite long operating times and further improvement relates to the corrosion resistance of electrodes.

Carbon nanotubes are modern materials for the realization of chemically stable, flexible, and transparent electrodes. CNT found its application in electronics in the development of light-emitting diodes, solar cells, field-effect transistors [9,10]. The chemical inertness of CNT is the most interesting property in application in perovskite light-emitting devices. Single-wall carbon nanotubes (SWCNTs) have several advantages over multi-wall carbon nanotubes (MWCNTs) like transparency, low resistivity but the cost of SWCNTs production is much higher than MWCNTs. Therefore, finding a way of implementing MWCNTs as an electrode will allow the development of stable, cost-effective, and flexible perovskite-based LECs.

2. Experimental section
2.1. Solution Preparation.
A CsPbBr$_3$ solution was prepared by dissolving PbBr$_2$ and CsBr with a molarity of 0.2 in an anhydrous DMSO solution. A polyethylene oxide (PEO) solution was prepared by dissolving 10 mg PEO ($M_w = 1$ 000 000 g/mol) in 1 ml DMSO, then the solution was stirred overnight at 60°C at 300 rpm. The perovskite-polymer solution CsPbBr$_3$:PEO (1:0.08 by weight) by mixing required masses of PEO and

Figure 1. a Single-layer LEC structure b The image of LEC.

Figure 2. a AFM height profile b AFM phase profile images of perovskite-polymer composite indicating partial coverage of perovskite grains by polyethylene oxide.
CsPbBr\textsubscript{3}. Next, to the perovskite-polymer solution required amount of LiTFSI solution DMSO (10mg/ml) to fulfill ratio 1:0.005 by mass. The resulting solution was stirred for 1 hour at 300 rpm.

2.2. Device fabrication.
LEC devices (Figure 1) were fabricated on a transparent, indium-tin oxide (ITO) coated glass substrate, deposition of perovskite-polymer composite was conducted in a nitrogen filled glovebox. Before deposition of the emission layer, the substrates were cleaned from various kinds of contaminants, after which they were subjected to thermal treatment and treatment in oxygen plasma for 10 minutes at 40 W. Cleansing consists of several stages. Each substrate was sequentially cleaned with a detergent solution, followed by a NaOH solution, deionized water, acetone, and isopropyl alcohol in an ultrasonication bath for 5 minutes. To obtain an emission layer with a thickness of 80 nm, the precursor solutions are centrifuged onto ITO substrates at 1000 rpm for 1 min., precursor solutions were spin-coated onto ITO substrates at 1000 rpm for 1 min. The film morphology was controlled by AFM spectroscopy (Figure 2). MWCNTs were used as a top electrode. Before deposition, MWCNTs are thermal treated at 100°C then treated with HCl vapor at 60°C, IPA was used for MWCNTs densification.

3. Results and discussion
Chemical treatment of CNT is a known method for purification and removal of different chemical impurities [11]. The removal of different residuals should affect the electronic properties of MWCNTs and the characteristics of perovskite LEC. Therefore, the study was carried out by measurement of IV, EL-V curves, and brightness for devices with MWCNT treated and non-treated with acid vapor, Figure 3 a and b shows obtained IV and EL-V curves. Application of a voltage of 0 V to 4 V corresponds to the case where ITO injects holes and MWCNTs injects electrons, applying a reverse voltage of 0V to -4 V corresponds to injection of holes from MWCNTs and electrons from ITO.

The applied bias voltage leads to an ion redistribution of perovskite and lithium salt in the perovskite film, cation ions drift to the cathode and form accumulation layer, and anions form the accumulation layer at an anode [5]. The formation of p-i-n structure and accumulation layers at the interface layers corresponds to the pinning of a Fermi level, which leads to the formation of ohmic contacts between electrodes and the perovskite-polymer layer. The formation of these ion accumulation layers leads to chemical interaction between ions and electrode material, moreover increased applied voltage can result in penetration of ions into the electrode, which is the main reason for electrode degradation [12].

The initial state of perovskite LEC shows visible electroluminescence (EL) when applied voltage higher than \(V_{th} = 2.4\) V, with and without acid vapor treatment (Figure 3a and b). Further successive I-V sweeps of the device without HCl vapor treatment demonstrate an increase of current below \(V_{th}\) region as well as in the higher \(V_{th}\) region, which is related to higher recombination via defects and loss of diode characteristic. After several voltage sweeps, the I-V curve loses its diode characteristic and becomes
more ohmic that results in the disappearance of EL (Figure 3a, gray and red curve). In contrast, the device with MWCNTs treated with acid vapors do not demonstrate a current increase in the whole voltage region and the I-V curve preserves its diode characteristic. After several repetition of voltage sweeps of both polarities, there is no degradation of the I-V characteristic and electroluminescence (Figure 3b). Figure 3b illustrated the dependences I-V and EL-V, according to which the treatment with acid vapors of MWCNTs avoids degradation of the devices and preserves electroluminescence for the subsequent application of a voltage of both polarities (Figure 3b). That allows achievement of luminance 516 cd/m². This difference in device operation can be related to acid cleaning of MWCNTs, which is a well-known method for MWCNTs cleaning from synthesis residuals and its functionalization.

4. Conclusion
We have shown that acid-treated MWCNTs can be used as a chemically stable top electrode of perovskite-based LECs. Initial MWCNTs contain many synthesis residuals that interact with perovskite ions and degrade device performance. Preliminary acid treatment of MWCNTs allows evading the degradation of perovskite LECs. The acid treatment removes residuals of MWCNTs production and allows preserve the diode characteristic of the device via suppression of defects development during accumulation of ions at the perovskite-MWCNTs interface. The use of acid vapor for MWCNTs treatment allows MWCNTs to be used as the top electrode for perovskite LECs.

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