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Influence of double layer PMHS/PDMS encapsulation on CsPbBr₃ PeLEC properties in high humidity conditions

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Abstract. In this paper we describe a new method to improve properties of a perovskite light-emitting electrochemical cell (PeLEC) by double layer polymer encapsulation. Our perovskite devices include 1) CsPbBr₃-poly(ethylene oxide) layer as emissive layer, 2) NiO_x:Cu nanoparticles layer as hole transport layer, 3) a transparent single wall carbon nanotubes as an electrode of the structure and 4) a double layer encapsulation polymer layers. These encapsulation layers consist of metal catalyst-free cross-linked polymethylhydrosiloxane and polydimethylsiloxane Sylgard 184. After 168 hours of aging in 80% relative humidity conditions an increase in luminance and in photo luminance quantum yield of our devices was detected. Our encapsulation provides optimal exposure of water vapor on perovskite material, which improves device properties by partial phase transition of CsPbBr₃ to Cs₄PbBr₆, which has been confirmed by X-ray diffraction method. The Cs₄PbBr₆ passivate CsPbBr₃ crystals and then the polymethylhydrosiloxane layer does not allow agglomeration of perovskite grains. The polydimethylsiloxane layer is required as a mechanical supporting layer. The polymethylhydrosiloxane/polydimethylsiloxane encapsulation of perovskite devices reveals a promising new way of development of flexible and stretchable perovskite light-emitting devices, which can work in extreme humid conditions.

Keywords: perovskite, encapsulation, polysiloxanes, metal-free cross-linking, humidity aging

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Материалы конференции

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Влияние двухслойной PMHS/PDMS инкапсуляции на свойства CsPbBr₃ PeLEC в условиях высокой влажности

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Аннотация. В данной работе описан новый метод улучшения свойств перовскитной светоизлучающей электрохимической ячейки путем двойной инкапсуляции в полимерные слои. Полученные перовскитные устройства содержат: 1) излучающий композитный слой CsPbBr₃-полиэтилен оксид, 2) дырочный транспортный слой наночастиц NiO_x:Cu, 3) электрод из слоя прозрачных одностенных углеродных нанотрубок, 4) инкапсулирующий двухслойный полимерный слой. Данный слой инкапсуляции состоит из слоя полиметилгидросилоксана, который имеет катализатор, не содержащий металлы, и полидиметилсилоксан Sylgard 184. После 168 часов выдержки в 80% относительной влажности было обнаружено увеличение численных значений люминесценции и квантового выхода фотолюминесценции полученных устройств. Предложенный способ инкапсуляции позволяет достичь оптимального воздействия паров воды на перовскитный материал, что способствует улучшению свойств устройств путем частичного фазового перехода из CsPbBr₃ в Cs₄PbBr₆, что было подтверждено методом дифракции рентгеновских лучей. Кристаллы Cs₄PbBr₆ обеспечивает пассивацию кристаллов CsPbBr₃, а инкапсулирующий слой полиметилгидросилоксана позволяет уменьшить агломерацию зерен перовскита. Слой полидиметилсилоксана выступает в роли поддерживающего механического слоя. Инкапсуляция в полиметилгидросилоксан/полидиметилсилоксан перовскитных устройств является перспективным направлением для разработки гибких и растяжимых перовскитных светоизлучающих устройств, которые могут работать в условиях повышенной влажности.

Ключевые слова: перовскиты, PeLEC, инкапсуляция, полисилоксаны, безметалльная сшивка, высокая влажность

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Introduction

The properties of optoelectronic devices based on perovskites are depended on environmental conditions. The effects of oxygen and humidity may worsen the properties of perovskite, causing degradation of the material [1]. The interaction of water with perovskites can lead to various phase transitions in the structure of perovskite or even its decomposition, which is accompanied by deterioration of optical and electrical properties [2].

There are many different methods of protecting perovskites from environmental influence. One of these methods is the encapsulation of perovskites in polymer materials. For example perovskite quantum dots encapsulated in poly(vinylidene fluoride) PVDF show less degradation when exposed to water [3]. Poly(methyl methacrylate) and polystyrene are also used as a protective material [4]. However, all these polymer materials have low flexibility, which limits their use in fabrication of flexible optoelectronic devices.

Among elastic polymers, it is possible to highlight dielectric, hydrophobic material - polydimethylsiloxane (PDMS), which has already been used to create flexible optoelectronic devices [5]. However, PDMS (commercially available Sylgard 184) causes perovskite material degradation due to cross linking mechanism by metal platinum catalyst. Silicon material for perovskite encapsulation should utilize a metal-free cross-linking mechanism. On the other hand, polymethylhydrosiloxane (PMHS) with a radical cross-linking mechanism does not require a metal catalyst.

Water, in addition to the negative effect of exposure to perovskite, may also improve the properties of perovskite. For example, water can be used to control the crystallization and synthesis of thin perovskite films [6]. In the presence of an optimal amount of water, the properties of perovskite materials can be enhanced [7, 8].

In this report we describe a method of improving the perovskite properties by device encapsulation in PMHS with a metal-free crosslinking method [9]. In addition to protecting the perovskite layer against the negative effects of humidity, the proposed encapsulation provides an improvement of the characteristics of the perovskite material by precise water vapor exposure.

Materials and Methods

For studying the influence of encapsulation two types of samples were fabricated. The first type is *films*, which consist of a perovskite layer on glass. Films without encapsulation, with PMHS encapsulation, annealed films without encapsulation were made. The second type is *devices*, which consist of indium tin oxide (ITO) (as a bottom electrode), nickel oxide nanoparticles layer (as a hole transport layer), perovskite layer, single wall carbon nanotubes pads (as a top electrode), and silver lacquer droplets (for better electrical contact).

Figure 1 shows the PeLEC device structure with a scanning electron microscope (SEM) image. Glass substrates with ITO were etched through a photoresist mask, which was made using an optical photolithography. After the patterned ITO has been formed, all substrates were cleaned in an ultrasound bath in deionized water, acetone, and isopropyl alcohol consequently.

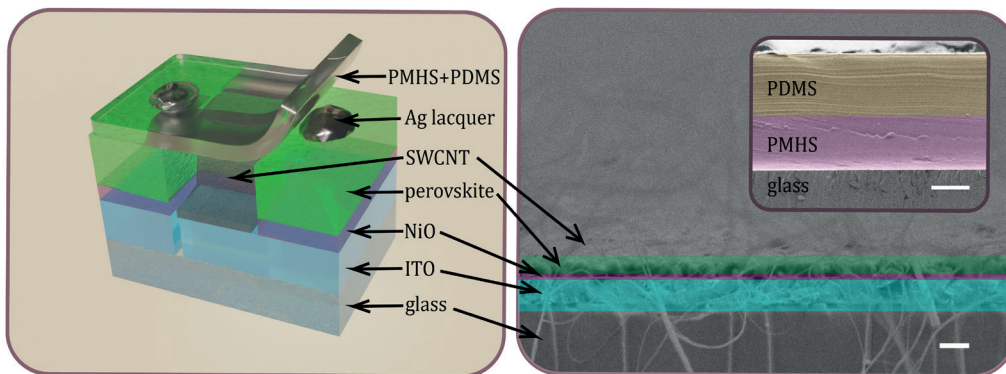


Fig. 1. Device structure with the SEM image

As a hole-transport layer (HTL) NiO_x :Cu nanoparticles were chosen. But before deposition of HTL all substrates had been dried and then were exposed to plasma treatment (2 min, 10 W).

To create the perovskite light-emitting layer, the 0.2 molar concentration perovskite solution was made, which contains a 1) solution of Cesium Bromide and Lead Bromide (II) salts (1:1), 2) a solution of PEO with molecular weight of 10^6 (20 mg/ml) and 3) a solution of lithium salts (10 mg/ml). DMSO was used as a solvent for all solutions. These three solutions were stirred at 300 rpm, 60 °C, 1 day. Then all solutions had been mixed and stirred at 300 rpm, 60 °C, 1 day. All solutions were made in a dry N_2 atmosphere in the glovebox system. Before forming perovskite, the sample surface was treated in oxygen plasma. The film was fabricated via composite solution drop-casting onto the activated sample surface. In the next step samples were spin-coated at 1000 rpm for 1 min. Then vacuum treatment was performed (10^{-3} bar, 1 min). In the final step samples were annealed (60 °C, 5 min).

As the top electrode of PeLEC single wall carbon nanotubes were used (80% transparency, sheet resistance 100 Ohm/square). Before placing the nanotubes pads the composite perovskite and NiO_x layers were mechanically removed from the target ITO surface areas. To form the contacts, nanotubes films were cut with a sharp blade into stripes and then transferred onto the target ITO surface using the dry-transfer technique. Anhydrous diisopropyl ether was used to densify the transferred nanotubes pads. In the final stage two conductive silver lacquer droplets were placed onto the anode and cathode areas of the patterned ITO layer for good electrical contact.

All devices were encapsulated in two steps. In the first step the mixture of PMHS and azobisisobutyronitrile (cross linking agent for PMHS) was spin-coated at 600 rpm for 60 sec and annealed at 80 °C for 5 hours on hotplate. In the second step PDMS was spin-coated at 800 rpm for 90 seconds and annealed at 80 °C for 5 hours. This double layer encapsulation was made at room relative humidity (< 50%). Figure 1 shows the thickness of PMHS and PDMS was 25 μm and 30 μm , respectively, which was measured by scanning electron microscopy.

To study the encapsulation all samples were characterized before and after stress-aging. The aging was conducted in dry N_2 atmosphere (0% humidity) for 40 days or high relative humidity conditions (80% humidity) for 168 hours, depending on the experiment.

To characterize optical properties of samples, spectra of absorption, transmission, photoluminescence and PLQY were measured. Also, to determine the optoelectronic properties, voltage-current density (J-V) and voltage-luminance (L-V) curves were obtained.

Results and Discussion

Figure 2 shows absorption, transmission, and PL spectra of nonencapsulated films (ref_film), encapsulated in PMHS film (PMHS_film), and annealed nonencapsulated film (a_ref_film). All spectra were normalized to ref_film. The PMHS encapsulated samples have no significant changes in the absorption, transmission and photoluminescence spectra compared to annealed samples without encapsulation. PMHS encapsulation prevents surface crystal grains agglomeration caused by a high-temperature film annealing.

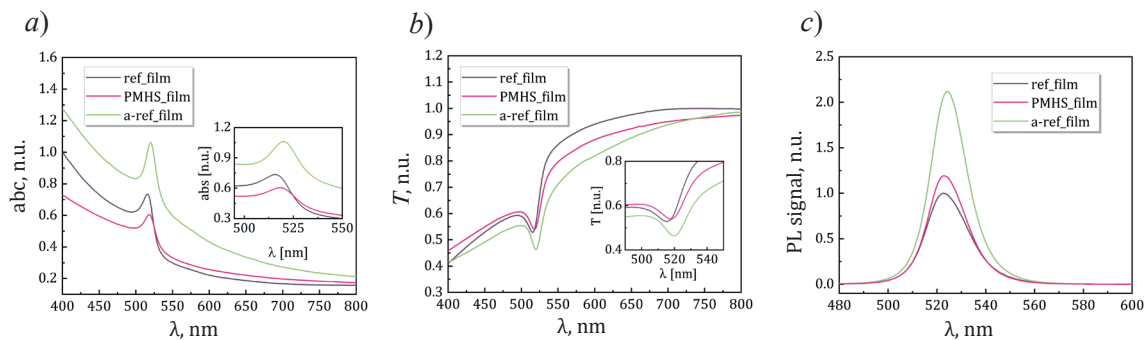


Fig. 2. Spectra of absorption (a), transmittance (b), PL for reference, encapsulated, and annealed films (c)

After aging in high-humidity conditions (80% humidity), the PLQY of encapsulated samples increased from $\sim 20\%$ to $\sim 50\%$, while for non-encapsulated samples, the PLQY value dropped by half to $\sim 10\%$ (as shown in Fig. 3, a). This can be explained by the formation of the Cs_4PbBr_6 phase, which passivates perovskite grains [10]. The formation of this phase was confirmed by X-ray diffraction (XRD) measurement (as shown in Fig. 3, b). Cs_4PbBr_6 phase may form due to water vapor exposure. But too much water vapor may decompose $CsPbBr_3$ to initial salts. We suggest that our method of encapsulation provides necessary balance.

For studying the encapsulation perovskite devices were characterized before and after aging in high-humidity conditions. For this research we fabricated nonencapsulated devices (ref_dev) and encapsulated in PMHS/PDMS devices (PMHS/PDMS_dev). Devices after aging have “h” as a prefix in name. For PMHS/PDMS_dev (encapsulated samples) an increase in the luminance value (from 1000 cd/m^2 to 2000 cd/m^2) was found after aging in high-humidity conditions (as shown in Fig. 3, c). Nonencapsulated devices lost their electroluminescence after aging. Encapsulated devices start emitting light at higher voltage after high-humidity conditions, which can be explained by increased serial resistance, because of partial phase transition $CsPbBr_3$ to Cs_4PbBr_6 .

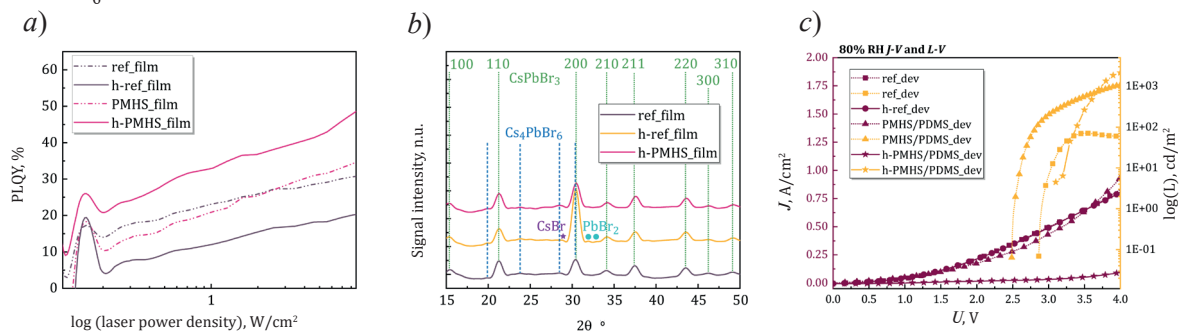


Fig. 3. Graphs of PLQY (a), XRD patterns (b), J-V and L-V curves (c)



Conclusion

We have described a method for improving CsPbBr₃ : PEO films and devices with a single-walled carbon nanotubes electrode by PMHS/PDMS encapsulation. Our double layer encapsulation prevents the interaction of perovskite and metal catalyst of PDMS, allows mechanical stability of the encapsulation layer, prevents surface crystal grains agglomeration, improves the properties of perovskite by providing a balance of water vapor exposure.

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