



CONFOCAL SPECTROMETER FOR STUDY OF ORGANIC-INORGANIC PEROVSKITES

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ABSTRACT

Organic-inorganic perovskites (OIPs) are promising photovoltaic materials due to the simplicity of synthesis technique and attractive physical properties. It is known that the power conversion efficiency of solar cells with an OIP photoabsorbing layer has recently reached approximately 23%. Unfortunately, OIPs easily degrade under influence of heat, moisture, oxygen and light soaking. Encapsulation of OIP layers to protect them against moisture and oxygen is necessary, which hampers to use traditional methods of analysis such as electron and probe microscopy, energy-dispersive X-ray analysis, X-ray photoelectron spectroscopy, X-ray diffraction, etc. As a result, significant difficulties in determination of photodegradation mechanisms arise, so, we are forced to look for other techniques of highly informative nondestructive analysis of such structures. For studying photoinduced processes in OIP layers, we applied confocal spectrometer, which allowed to use a laser beam (i) as a source of optical radiation causing photodegradation; (ii) for the local analysis of changes in the structure of the area exposed to optical radiation using Raman and photoluminescence (PL) spectra; (iii) for local measurement of solar cell parameters (short circuit current, open circuit voltage). The presence of a 3D piezoelectric scanner enables one to do the mapping of spectral and photoelectric parameters, which is important for establishing the homogeneity of the objects under study. The proposed approach allows obtaining information on the phase composition and spectrum of electronic states (from the Raman and PL spectra), as well as on the dynamics of charge carriers. By recording PL and Raman spectra, short circuit current and open circuit voltage under laser beam illumination, one can observe the evolution of the system in the online mode, which gives information regard to processes occurring in the OIPs when they are illuminated.

Keywords: confocal spectrometer, nondestructive analysis, organic-inorganic perovskite, photoluminescence

1. INTRODUCTION

Hybrid organic-inorganic perovskite solar cells (SCs) appeared less than 10 years ago [1] and immediately attracted special attention because they combine a high light absorption coefficient, band gap energy close to the optimal value, a long lifetime of charge carriers (up to microsecond range), and the possibility of low temperature (not more than 100 °C) solution based synthesis [2-5]. It is interesting to note that the efficiency of perovskite SCs (PSCs) increased in a short period of time to more than 23%, which is associated with the possibility of varying the architecture, as well as the chemical composition of the perovskite and transport layers [6-8]. However, there is a problem in the way of commercialization of such solar cells, which is associated with rapid degradation under the influence of light, heat, atmospheric moisture and oxygen [9-13]. The variation of chemical composition of the perovskite structure, electron and hole acceptor layers, as well as encapsulation made it possible to achieve significant resistance to moisture, oxygen and heat [14]. However, photodegradation still remains an unresolved problem, since regeneration in the dark [15] is too slow to completely restore operating parameters decreased after the light exposure in real operating conditions [14]. Thus photovoltaic researchers focus on identifying the regularities of photodegradation and regeneration of PSCs, establishing the mechanisms responsible for these processes, and also searching for ways to reduce the rate of degradation [4]. The experimental study of PSCs is complicated by difficult access to the active area of device (perovskite and acceptor layers) due to the presence of encapsulation. This makes it problematic to use traditional methods of analysis (X-ray diffraction analysis, scanning electron and probe microscopy, photoelectron



spectroscopy) and requires development of techniques based on other non-contact analytical methods, one of which can be the optical confocal spectroscopy.

The aim of our work was the development of a technique for studying photosensitive semiconductor structures using a confocal spectrometer. The objects of research were organic-inorganic PSCs with different chemical composition of perovskite layer. The proposed technique makes it possible to use the laser beam of the spectrometer not only (i) for excitation the Raman and photoluminescence (PL) spectra, but also (ii) for local measurement of photoelectric parameters of SCs (short-circuit current, open-circuit voltage); as well (iii) as a source of local photodegradation for establishing the dynamics of the PSCs properties under illumination. The presence of a 3D-piezoscanner allows mapping of spectral and photoelectric parameters, which is important for unraveling the degree of spatial homogeneity of the samples. So, using of the confocal spectrometer allows obtaining extensive information on photodegradation and recovery processes by analyzing the phase composition and the spectrum of electronic states (from Raman and PL spectra), as well as the generation, transport and recombination of charge carriers. In particular, the registration of PL spectra, short-circuit current and open circuit voltage during illumination with a laser beam for a long period of time enables one to observe the evolution of the system in real time, which gives an information about the processes occurring in solar cells during their illumination.

2. METHODOLOGY

The method of PSC preparation is described in [15]. Briefly, the studied organic-inorganic perovskite SCs contained MAPbI₃, (Cs/FA)Pb(I/Br)₃ or (Cs/FA/MA)Pb(I/Br)₃ as absorbing layer, where MA is methylammonium (CH₃NH₂), and FA is formamidine (CH₄N₂). SnO₂ and Spiro-MeOTAD were used as electron-acceptor and hole-acceptor layers, respectively; ITO and Au were used as front and back contacts.

Nanofinder HE confocal spectrometer (LOTIS TII, Belarus-Japan) was used in the study. As PbI₂ is known as the main product of OIP decomposition, we used a 4 μm thick PbI₂ film as the reference sample. Parameters of Raman spectra measurement were the following: the wavelength of the exciting light $\lambda = 532$ nm, the width of the spectrometer pinhole $ph = 100$ μm, the diffraction grating constant $d = 600$ mm⁻¹ (which provided a spectral resolution of 2.5 cm⁻¹), the exciting radiation power $P = 6$ μW, the diameter of laser spot on the sample $D = 2$ μm (10x objective with numerical aperture NA = 0.3), signal accumulation time $t = 120$ s. These parameters were chosen in such a way as to exert no destructive effect on the objects of investigation. Before and after measurement of Raman spectrum, PL spectra were recorded under the conditions described in the next section. The identity of the shape and position of the obtained Raman and PL spectra made it possible to conclude that the method is non-destructive.

PL spectra were measured in the following conditions: excitation light wavelength $\lambda = 532$ nm, width of the spectrometer pinhole $ph = 25$ μm, grating constant $d = 600$ mm⁻¹ (which provided a spectral resolution better than 0.1 nm), the power of the exciting radiation $P = 0.6$ μW, the diameter of laser spot on the sample $D = 2$ μm (10x objective, NA = 0.3), the signal accumulation time $t = 5$ s. For observation of evolution of PL spectral parameters, exposure time was chosen equal to 250 s (50 PL spectra). Taking into account the used optical power (0.6 μW), such exposure roughly corresponded to the one day illumination of the solar cell under actual operation conditions. The power of the laser radiation was chosen in such a way as to exert no destructive effect on the sample, but at the same time to provide a slight effect, which makes it possible to detect the behavior of the object under local illumination. For analysis of spatial homogeneity, scanning of samples using a 3D-piezoscanner was carried out with taking PL spectra in each point under the same measurement conditions.

Short-circuit current (SCC) and open-circuit voltage (OCV) were measured when recording PL spectra with a Keithley 2400 source meter.

3. RESULTS AND DISCUSSIONS

3.1. Individual Capabilities of Confocal Spectrometer

Confocal spectrometer is the useful tool for non-destructive analysis, which does not require special sample preparation and allows studying encapsulated samples like perovskites. This section is devoted to the analysis of confocal spectrometer capabilities without any additional devices.

3.1.1. Raman Spectra

Traditionally, confocal Raman spectroscopy is used for local qualitative determination of the phase composition of the samples under study. In the case of OIPs, sharp Raman peaks can be observed only at low temperatures, which is impossible for encapsulated samples due to the risk of encapsulation damage. However, Raman spectroscopy can be used, for example, to identify the presence of the PbI_2 phase as the most common product of perovskite degradation. We investigated weakly and strongly degraded PSCs based on $(\text{Cs}/\text{FA})\text{Pb}(\text{I}/\text{Br})_3$ and $(\text{Cs}/\text{MA}/\text{FA})\text{Pb}(\text{I}/\text{Br})_3$ layers.

Figure 1 presents the obtained Raman spectra of reference PbI_2 film and PSCs based on $(\text{Cs}/\text{MA}/\text{FA})\text{Pb}(\text{I}/\text{Br})_3$ perovskite previously degraded under the influence of prolonged light exposure and increased temperature in natural condition. The obtained spectra of PbI_2 and perovskite have the shape very similar to that observed in many works [16, 17]. The spectra are given in arbitrary, but in the same units. The absence of Raman lines inherent to PbI_2 in spectrum for perovskite film allows to exclude formation of lead iodide as a process which takes place in our particular case of white light exposure degradation is not accompanied by formation of lead iodide.

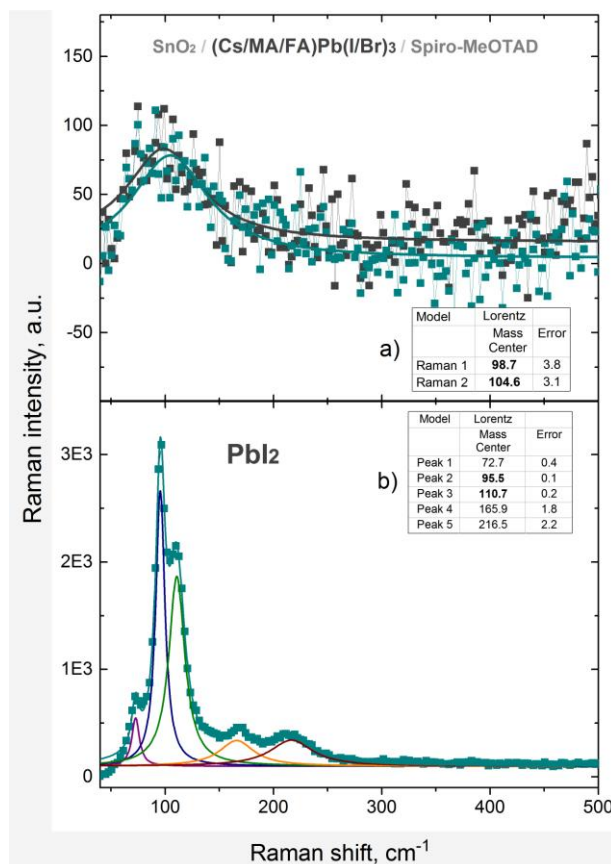


Fig. 1. Raman spectra of degraded $(\text{Cs}/\text{MA}/\text{FA})\text{Pb}(\text{I}/\text{Br})_3$ (a) and reference PbI_2 films (b)

3.1.2. Photoluminescence Spectra and Mapping

It is known that hybrid organic-inorganic perovskites can contain more than one species of ions in the cation and anion sublattices for better photovoltaic properties and stability [14]. However, in the case of perovskites with a complex composition, multiphase heterogeneous systems are often formed. Obviously, in this case several peaks corresponding to the individual phases located in the confocal volume will be observed in the PL spectrum. Thus, the registration of PL spectra is a simple method which allows to identify the phase composition of the object under study.

The characteristic PL spectrum of $(\text{Cs/FA})\text{Pb}(\text{I/Br})_3$ based PSC is shown in Fig. 2. A single symmetrical peak corresponding to interband radiative recombination in the perovskite layer indicates the presence of a single phase characterized by a definite value of the PL mass center (774 nm) from which the value of the band gap can be approximately estimated (1.60 eV) in the investigated samples. The obtained PL spectra of perovskite have the shape very similar to that observed in other works [18]. The obtained PL spectra not only characterize the quality of the initial sample, but also help to track the possible formation of secondary phases at different stages of the life cycle of the SCs. Determination of the degree of spatial homogeneity is an important stage in the primary characterization of samples, since photodegradation is carried out by illuminating the working surface of the PSCs, whose dimensions are 1000 times larger than the diameter of the laser beam, by which the Raman and PL spectra are recorded. Therefore, without the analysis of spatial homogeneity, the results can be contradictory, and the resulting conclusions are incorrect. The detection of the scattering of the parameters of PL spectra, such as the intensity and center of mass (inset in Fig. 2), allows one to judge the spatial arrangement of the centers of non-radiative recombination, the distribution of regions with the greatest and the least efficiency of charge carrier extraction by transport layers and spatial homogeneity of the chemical composition.

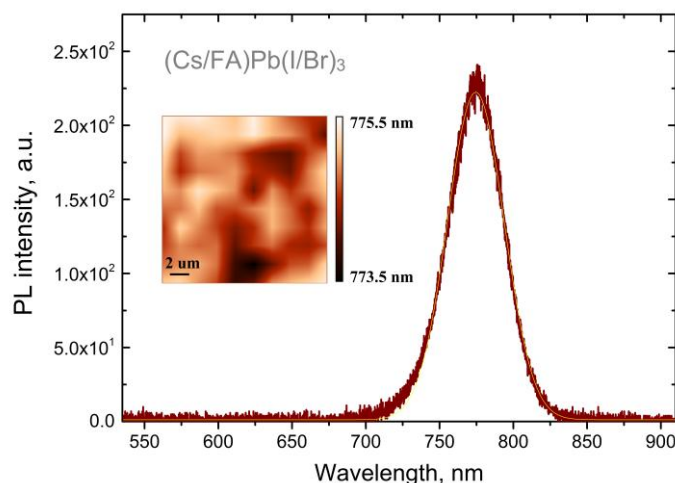


Fig. 2. Typical PL spectrum of $(\text{Cs/FA})\text{Pb}(\text{I/Br})_3$ SC and mapping of PL peak position for $20 \times 20 \mu\text{m}^2$ region (inset)

3.1.3. Kinetics of PL Spectra Parameters

Individual PL spectra do not give a complete information about the processes occurring in the solar cell during its illumination. In addition, at different stages of the life span of the PSCs, certain parameters, for example, the intensity or position of the mass center of the PL band may be identical, while the rates of change of these parameters may differ, since different processes will be responsible for their change. Recording photoluminescence spectra at the equal time intervals, we can observe the evolution of PL parameters during illumination. As one can see from Fig. 3, light-

induced processes in general case can lead both to increasing and decreasing PL intensity, which is related to competition of creation and deactivation of recombination centers.

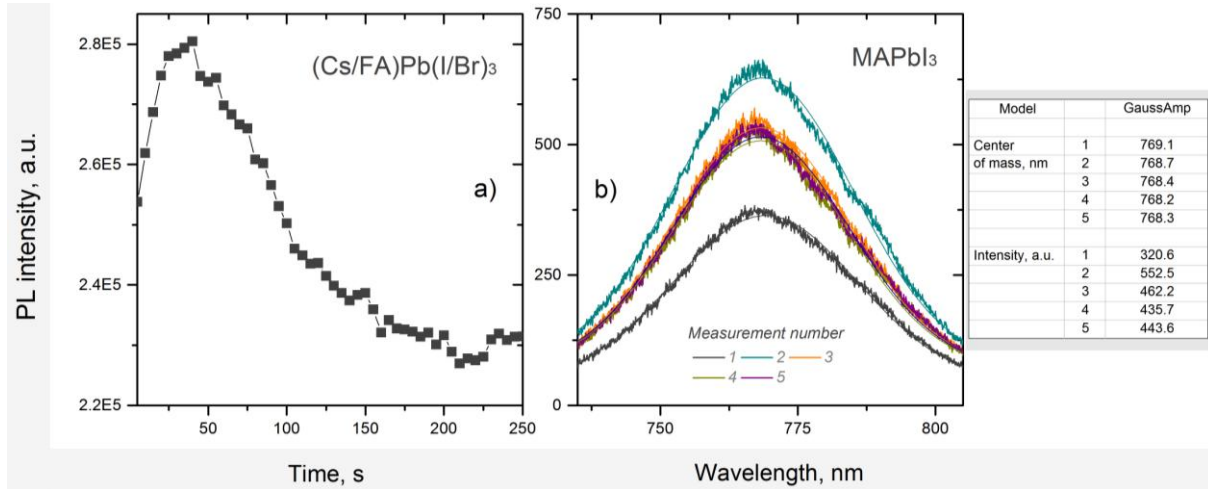


Fig. 3. PL kinetics for (Cs/FA)Pb(I/Br)₃ PSC (a); PL spectra consequently measured for MAPbI₃ PSC (b)

3.2. Capabilities of Confocal Spectrometer with Additional Devices

The consideration given above demonstrates how much information can be obtained using solely confocal spectrometer. However, changes of PL intensity or mass center do not give complete information about the behavior of charge carriers in the sample and, in particular, about peculiarities of their recombination. So, additional devices for measurement of electrical parameters allow to distinguish this processes.

3.2.1. Short-Circuit Current and Open-Circuit Voltage

Advantages of using confocal spectrometer for determination of SCC and OCV are the possibility of simultaneous measurement of PL spectra, which allows to describe the recombination processes in the photoabsorbing layer more accurately. As an example, Fig. 4 shows the kinetics of the change in the OCV, SCC and PL intensity. Approximation of the obtained kinetics by the exponential function (Fig. 4) demonstrates the equality of the characteristic times (~ 16 s) of the processes responsible for the initial decrease in the PL intensity in the short-circuit mode and the increase in the open-circuit voltage, which can be explained by the process of charging the cell capacitance of a locally photogenerated charge carriers. The constancy of the short-circuit current indicates that the processes leading to a decrease in the PL intensity are not associated with the formation of defects at the interfaces.

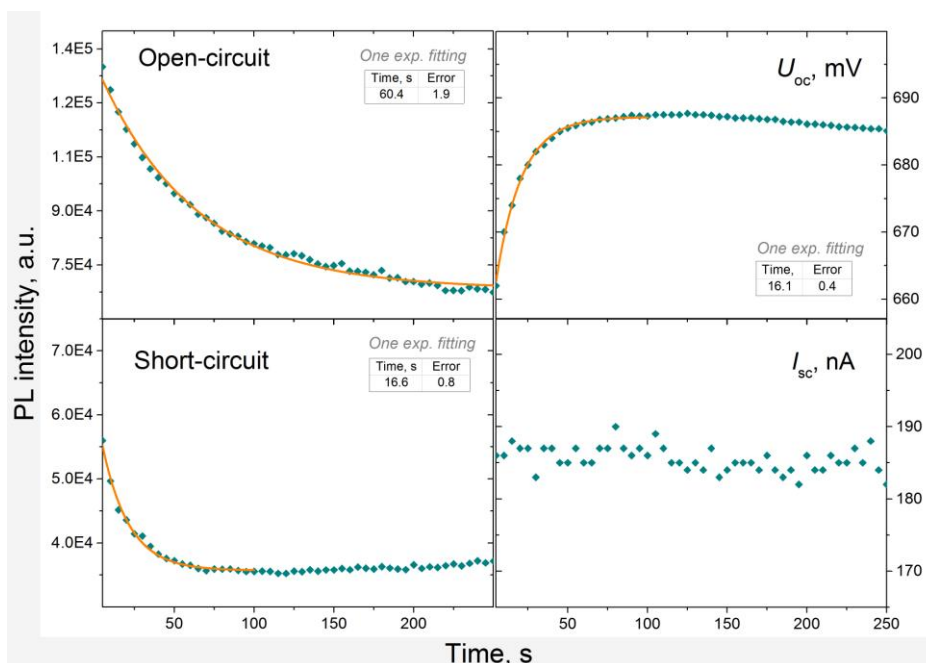


Fig. 4. Kinetics of PL intensity, OCV, SCC for $(\text{Cs/FA})\text{Pb}(\text{I/Br})_3$ based SC and their fitting with exponential function

4. CONCLUSIONS

Presented capabilities of confocal spectrometer allow to conclude that the developed and approved method of local investigation of photosensitive structures (by example of organic-inorganic perovskite solar cells) based on the use of a confocal spectrometer and allowing to measure the Raman and PL spectra, kinetics of PL parameters, short-circuit current, open-circuit voltage under the influence of monochromatic radiation can be used for the analysis of photosensitive structures of various types.

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