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Optical properties of PZN-PT nanoparticles thin layer on ITO glass for photovoltaic application

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Abstract: In this work, undoped and Mn doped $Pb(Zn_{1/3}Nb_{2/3})O_3$-4.5$PbTiO_3$ nanoparticles were dispersed in biopolymer and in mixed biopolymer + pentacene as active layer and deposited by spin coating on ITO glasses. Morphological, optical and electrical properties of these layers were investigated. SEM images show the superposition of different deposited layers ITO/TiO2/PZN-PT-np-biopolymer on glass substrate with thicknesses of 1.600 µm, 1.505 µm and 1.765 µm respectively. The absorbance value in UV visible for pentacene layer increases from 75 % to 99 % while the transmittance for ITO glasses diminishes from more than 80 % to 2 %. Optical gaps of ITO, TiO_2, PZN-PT nanoparticles are respectively 3.75 eV, 3.2 eV and 3.15 eV. Pentacene deposition reduced the gap to 1.65 eV for undoped sample and 1.60 eV for the doped ones. Intermediate gaps (2.3 eV and 2.6 eV for undoped sample and 2.15 eV and 2.7 eV for doped sample) were observed. Photoluminescence performed between 450 nm and 750 nm confirms « these intermediate gaps ».

Keywords: PEROVSKITE, NANOPARTICLES, THIN FILM, OPTICAL PROPERTIES, BAND GAP

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Introduction

Among all the solution-processed thin film optoelectronic material technologies investigated over the past 2 decades, organic–inorganic (or hybrid) methylammonium lead tri-iodide (MAPbI3) perovskites have emerged as clear front-runners with proof-of-concept high performance devices demonstrated for a broad range of applications [1-8]. The MAPbI3-based photovoltaic devices have demonstrated constantly increasing power conversion efficiency (PCE), which now exceeds 22% [9-10] and is steadily approaching that of single-junction monocrystalline Silicon (c-Si) solar cells. Although the record for the highest efficiency perovskite solar cell was achieved using a mesoporous titania (TiO_2)-based architecture [10-12] photovoltaic devices employing a simple planar architecture are closing in with the highest reported efficiency of 20% [6, 13, 14]. Despite this breakthrough, hybrid lead-halide perovskites are known to degrade due to moisture and heat, upon prolonged exposure to light and are prone to ion or halide vacancy migration, leading to unstable operation of photovoltaic devices. Great efforts have been put forth for achieving highly efficient planar solar cells by exploring for potential ideal contact layers [15]. In addition, it is now realized that the next steps in advancing hybrid perovskite-based materials toward a viable photovoltaic technology will require simultaneously improving both the overall efficiency and also intrinsic stability. To overcome such difficulties, we oriented our research to inorganic PZN-PT perovskite materials with excellent and stable properties compared to the organic-perovskite ones. However, despite their excellent properties, one of the greatest difficulties to integrate widely such materials in electronic devices is to achieve them in thin films form because of their incongruent melting property. In this paper, undoped and Mn doped PZN-4.5PT nanoparticles were dispersed in biopolymer and in mixed biopolymer + pentacene as active layer and deposited by spin coating on ITO glasses. After the successful deposition of the thin film, morphological, optical and electrical properties were investigated.

Experimental procedure

The quality of the layers depends strongly on the state of the materials surfaces and their interfaces, whether organic-organic or metal-polymer. Thus a chemical treatment of the ITO substrate surface is necessary to eliminate the contaminating elements. For this, we combined the ultrasonic method with piranha to clean substrates. The piranha solution is composed of H_2SO_4 96 % (30 ml) and H_2O_2 (10 ml). After cleaning, the different layers, namely titanium oxide (TiO_2), undoped and Mn doped PZN-4.5PT nanoparticles dispersed in a biopolymer and pentacene were successively deposited by spin coating. In this study we used a natural biopolymer containing polysaccharides with short side chains. This polymer can take several conformations that allow it to adapt or intercalate depending on the environment.

Colloidal suspension of TiO_2

The titanium oxide used in this study is a finished product marketed by Sigma-Aldrich (CAS number 13463-67-7). The suspension is obtained by grounding TiO2 powder in a mortar and adding a few drops of acetic acid giving a white paste. The as prepared paste is deposited on ITO glass substrate at room temperature using a spin coater Midas 1200D at 3500 rpm with an initial acceleration of 5 seconds and an operating time of 2 min.

PZN-PT nanoparticles thin film fabrication

Undoped and Mn doped PZN-4.5PT single crystals synthesized by the flux method [16] were grounded in a mortar to obtain a very fine powder (TEM characterizations revealed nanoparticles of the nanometer order and studies (not shown here) have confirmed that the population of spherical particles having a diameter of 30 nm was more representative). The grounded powder was dispersed in biopolymer solution. To obtain a homogeneous film, spin coating process was carried out at room temperature at 3500 rpm with an initial acceleration of 5 seconds and an operating time of 10 min. The biopolymer is used to disperse undoped and Mn doped PZN-4.5PT perovskite nanoparticles but also as a hole-injecting layer through the organic layer/ITO interface. Secondly it serves buffer layer to prevent diffusion of oxygen and indium to active layer, these impurities can act as exciton recombination centers or photogenerated traps carriers.

Results and discussion

SEM images

Surface morphology was observed by using an electron beam lithography system Pioneer Raith model in C(PN)2 (Paris 13 University). Observation of film surfaces in a scanning electron microscope makes it possible to verify the homogeneity of films, grains shapes and aggregates as well as the qualitative analysis of layers.

SEM images of samples composed of ITO/TiO2/PZN-PT-np-biopolymer films (DKRN-ITO2), ITO/TiO2/PZN-PT+1%Mn-np-biopolymer (DKRN-ITO4), ITO/TiO2/PZN-PT-np-biopolymer/pentacene (DKRN-ITO7), ITO/TiO2/PZN-PT+1%Mn-np-biopolymer/pentacene (DKRN-ITO8) deposited at room temperature on glass substrates are shown respectively in figure 1. DKRN-ITO2 and DKRN-ITO4 (Fig. 1a and 1b) shows a homogeneous, sparse and porous surface, showing white gray coloured non-regular agglomerated grains with an average size of 30 nm. DKRN-ITO7 and DKRN-ITO8 samples (Fig. 1c and 1d), developed in the same conditions with the only difference of adding a pentacene layer, have uniform, compact and homogeneous slightly black surfaces. This suggests that pentacene leads to a coalescence of the grains by diffusion through the pores. The morphology of the surface is initially related to the energy of the particles. Indeed, when the particle on the substrate acquires a great energy, it will have a large surface diffusion length. Then, this allows it to reach the sites energetically favorable and thus to

complete the possible gaps, reducing the irregularities of the surface. In the other case, the particles deposited on the substrate in contact with the air having lost a large part of the energy, their diffusion length will be very short. Therefore, the morphology of the surface will reflect a part of the morphology of the substrate but with greater irregularities due to the shading effect, and secondly the nature of the deposited material [17].

Observation in scanning electron microscope in transverse mode, allowed us to see the disposition of the various deposited layers but also to determine their thickness. For example, in figure 2a showing the SEM image in transverse mode of the DKRN-ITO2 sample composed of the ITO / TiO2 / np-PZN-4.5PT-biopolymer layers, we obtained thicknesses of 1.600 µm, 1.505 µm and 1.765 µm respectively for ITO, TiO_2 and np-PZN-PT-biopolymer. This allowed us to confirm the value of the thickness of the ITO given by the supplier (1.600 µm).

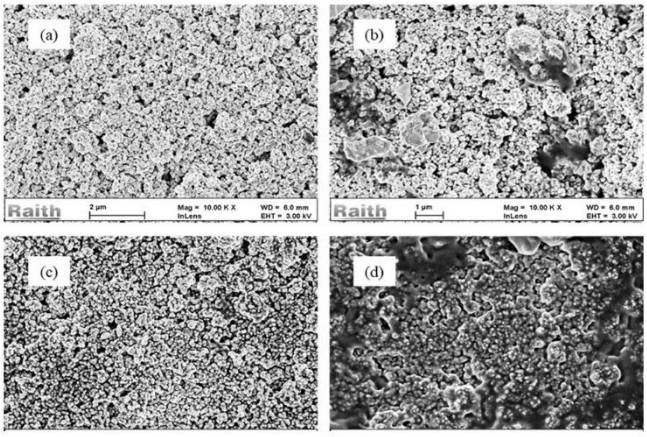

Figure 1: SEM Images of thin film (a) DKRN-ITO2, (b) DKRN-ITO4, (c) DKRN-ITO7 and (d) DKRN-ITO8

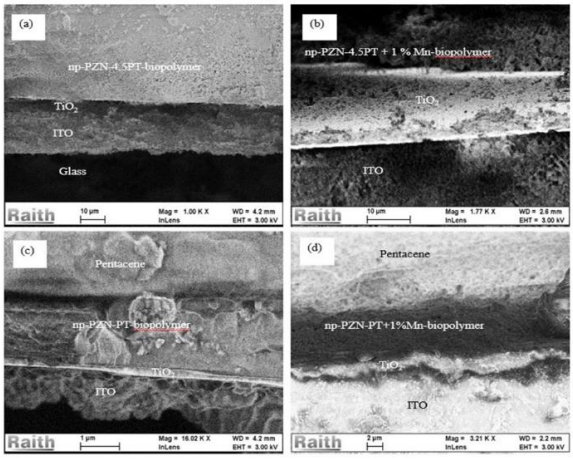

Figure 2: SEM Images in transversal mode (a) DKRN-ITO2, (b) DKRN-ITO4, (c) DKRN-ITO7 and (d) DKRN-ITO8

Table 1: Thickness values of different layers

Thicknesse (µm)	ITO	TiO_2	Biopolymer	Pentacene
DKRN-ITO2	1,600	1,505	1,765	-
DKRN-ITO4	1,600	2,401	1,667	-
DKRN-ITO7	1,600	1,709	1,680	1,431
DKRN-ITO8	1,600	1,691	1,582	1,322

Optical properties

Optical properties of thin films were investigated using an UV-Visible spectrophotometer with an integrating sphere model LAMBDA 950S in IM2NP (Marseille). Measurements are made with a pitch of 5 on a wavelength spectrum ranging from 250 and 1500 nm.

Transmittance and absorption

Typical transmission spectra obtained for the different deposited layers at room temperature are shown in figure 3a. For the ITO reference sample composed of ITO layer only, there is a strong transmission of more than 80 % throughout the visible band. This confirms the transmission value given by the supplier. This transmission decreases with the deposition respectively of TiO2/np-PZN-4.5PT-biopolymere, TiO2/np-PZN-4.5PT+1%Mn-biopolymer, TiO2/np-PZN-4.5PT-biopolymere/pentacene and TiO2/np-PZN-4.5PT+1 %Mn-biopolymer/pentacene.

For the different deposits, the general patterns of the spectra are similar. Two transmission domains can be distinguished according to the wavelength:

- A domain (λ < 800 nm) characterized by high absorption and low transmission of the different layers, which corresponds to the absorption of the layer in question.

- A relatively high transmission domain for λ range of 800 - 1500 nm, it increases sharply and tends to values between 30 and 56 % for the DKRN-ITO2 sample, 26 and 47 % for the DKRN-ITO4 sample, 25 and 45 % for the DKRN-ITO7 sample, 45 and 70 % for the DKRN-ITO8 sample. Authors in the literature, such as D. Kobor [18] report transmission values of 25 and 45 % for wavelengths between 600 and 900 nm of PZN-4.5PT single crystals. This confirms the values obtained in this study, although we can also consider the influence of the organic layers of biopolymer and pentacene which tend to attenuate this transparency. In figure 3b, it can be seen that the addition of the pentacene layer greatly increases the absorption throughout the visible spectrum. It is deduced that

pentacene increases the absorption band in the visible (~ 90 %). Indeed, pentacene is a semiconductor that absorbs well in the visible and authors like A. Skaiky [19] have shown it. This is a good thing for photovoltaic applications. On the other hand, the biopolymer seems to have less influence on the absorption compared to pentacene.

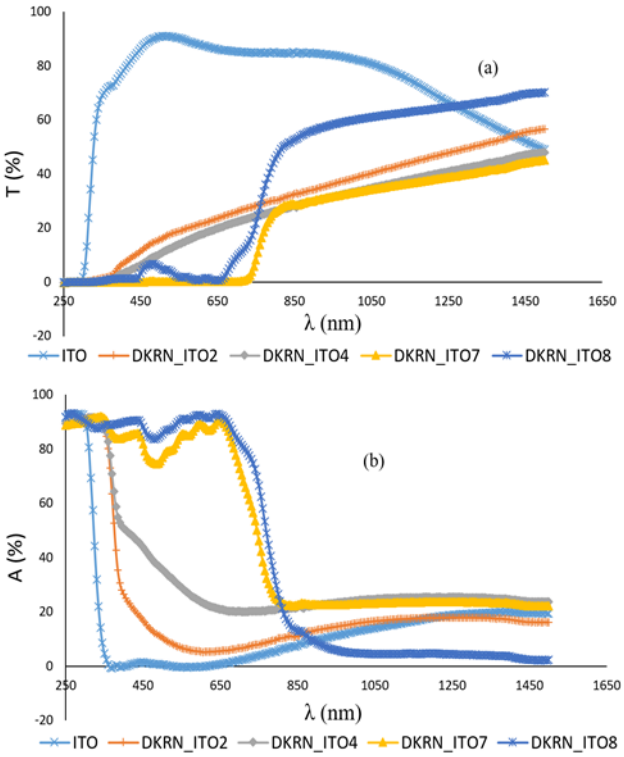

Figure 3: (a) transmittance and (b) absorbance according to the UV-Visible-NIR wavelength for different samples

Determination of band gap

To calculate the optical gap Eg, we used Tauc relation [20].

$$\alpha h\nu = A(h\nu - E_g)^n \qquad (1)$$

Where A is a constant, hν is photon energy, E_g is the allowed energy gap, n = ½ for allowed direct transition, α is the absorption coefficient and n = 2 for allowed indirect transition.

Thus, from the value of the absorption coefficient and by plotting the curve of $(\alpha h\nu)^2$ as a function of the photons energy, we have determined the optical gap Eg: it suffices to draw the slope in the region of absorption as shown in figure 4 and the intersection of this line with the abscissa axis (for αhν = 0) gives directly Eg. The values found are shown in table 2.

For the ITO reference sample, the value of the gap found (3.75 eV) is in perfect correlation with that found by G. Fatma-Zohra [21] (3.80 eV). For the DKRN-ITO2 and DKRN-ITO4 samples, the gap remains high with values of 3.20 eV and 3.15 eV that can respectively correspond to the TiO_2 gap that is 3.02 eV according to Schon [22] and PZN-PT gap equal to 3.04 eV according to He Chong-Jun [23]. Pentacene deposition reduced the gap to 1.65 eV for the DKRN-ITO7 sample and 1.60 eV for DKRN-ITO8. We also note the presence of intermediate gaps (2.30 eV and 2.60 eV for DKRN-ITO7 and 2.15 eV and 2.70 eV for DKRN-ITO8). These intermediate gaps could be due to the heterogeneity of the layers (presence of TiO_2, nanoparticles of PZN-4.5PT undoped or doped Mn, biopolymer, pentacene). These values could correspond respectively to the gap of the pentacene layer (1.65 and 1.60 eV), the combination of the biopolymer with pentacene (2.30 and 2.15 eV) and TiO_2 (2.60 and 2.70 eV). It appears from the results that pentacene tends to influence even the gap of the inner layers (TiO_2, nanoparticles and biopolymer) whose absorption is considerably reduced. The results are in perfect correlation with the curves of figure 3.

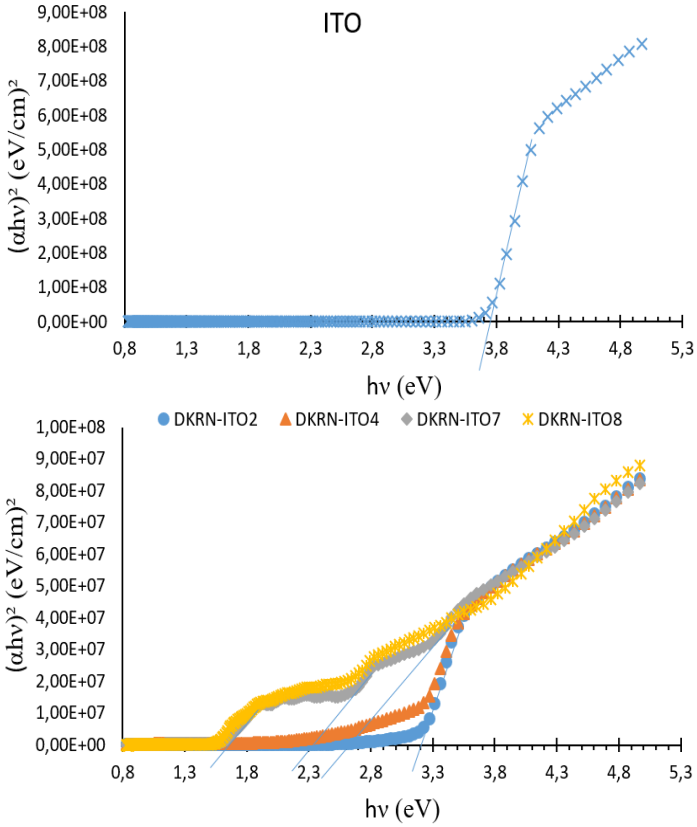

Figure 4: Tauc plot curves of (x) ITO, (●) DKRN-ITO2, (▲) DKRN-ITO4, (◆) DKRN-ITO7 and (✳) DKRN-ITO8

Table 2: Gap values of different samples

Samples	E_{g1} (eV)	E_{g2} (eV)	E_{g3} (eV)
ITO	3,75	-	-
DKRN-ITO2	3,20	-	-
DKRN-ITO4	3,15	-	-
DKRN-ITO7	1,65	2,30	2,60
DKRN-ITO8	1,60	2,15	2,70

Photoluminescence

To confirm the effect of pentacene on the reduction of the optical gap, we investigate photoluminescence on samples DKRN-ITO7 and DKRN-ITO8. Figure 5 shows the photoluminescence (PL) spectra obtained. We observe a first emission peak at 2.3 eV and a second peak at 2.5 eV for DKRN-ITO7 while for DKRN-ITO8 we have a peak at 2.2 eV and another at 2.6 eV. This confirms the values of the intermediate gaps found by the Tauc method. Photoluminescence was performed between 450 nm and 750 nm. This does not allow observing the peak of 1.6 eV revealed by the method of Tauc. Indeed, this peak would probably appear in the infrared.

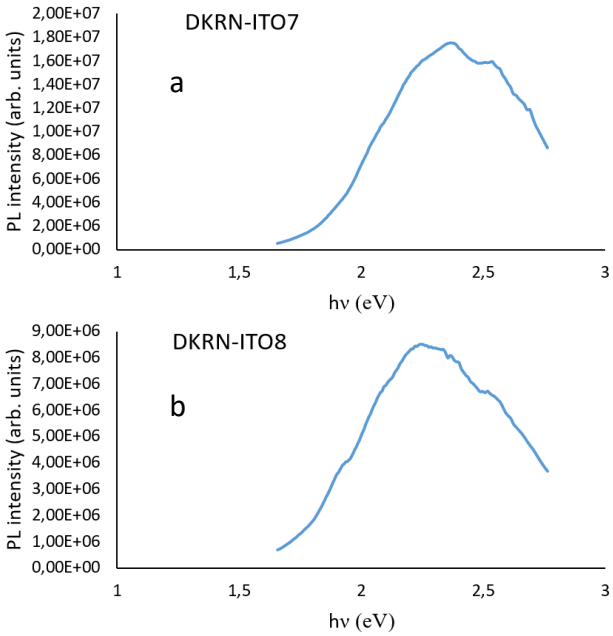

Figure 5: Photoluminescence of (a) DKRN-ITO7 and (b) DKRN-ITO8

Conclusion

PZN-4.5PT nanoparticles thin layers were successfully prepared using a biopolymer. SEM images revealed the superposition of different deposited layers. It shows uniform, compact and homogeneous surface with deposition of pentaconene layer. Optical characterization by transmittance and absorbance measurements allowed us to observe the influence of the layers on absorption and optical gap. It also made it possible to follow the evolution of the gap according to the nature of the deposited layer. Pentacene has been very successful in improving photovoltaic properties.

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