Research Article

Double-Layered Zirconia Films for Carbon-Based Mesoscopic Perovskite Solar Cells and Photodetectors

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Carbon-based mesoscopic perovskite solar cells (PSCs) and photodetectors were fabricated with the application of double-layered ZrO_2 films, consisting of zirconia nanoparticles and microparticles for the first and the second layer, respectively. This assembly exploits the ability of the zirconia microparticles to scatter and hence diffuse the incident light, causing a more efficient illumination of the perovskite layer. As a result, the photocurrent densities produced by a photodetector and a carbon-based PSC were increased by nearly 35% and 28%, respectively, compared to devices assembled using a conventional single zirconia film. Following the increase in the photocurrent, the responsivity of the photodetector and the power conversion efficiency of the PSC were increased analogously, due to the improved light harvesting efficiency of the perovskite layer. Parameters, such as the total thickness, the roughness, and the crystallinity of the films, were examined. Differences in the grain size and in the crystal planes of the perovskite were observed and evaluated. These results demonstrate that a double-layered ZrO_2 film can enhance the efficiency of solar cells and photodetectors, enhancing the prospects for their potential commercialization.

1. Introduction

Solar cells based on organolead halide perovskites (PSC) have attracted the intense interest of researchers worldwide during the last several years. This intensive research work has led to certified power conversion efficiencies exceeding 20% [1, 2]. The main component of these devices is the perovskite layer, acting both as a light harvester and charge transport material. The high efficiency obtained arises from the excellent optoelectronic properties of the perovskite layer, such as high absorbance of the incident light over a broad range covering the visible and the near-infrared spectrum, long carrier diffusion length and high carrier mobility, transport of both electrons and holes, and low exciton binding energy [3–6].

Several device architectures have been proposed up to now in an effort to achieve increased efficiency [3, 7, 8]. Among them, the carbon-based mesoscopic perovskite solar cells offer a promising solution towards potential commercialization

[6, 8]. A typical solar cell consists of a transparent conductive glass electrode (FTO or ITO), an electron transport layer (ETL, usually TiO_2 or ZnO), a layer based on ZrO_2 or Al_2O_3 acting as a spacer, and finally a carbon electrode (Figure 1) [9, 10]. The various layers are mesoporous and are deposited sequentially on top of each other, followed by high-temperature annealing. Finally, the perovskite penetrates inside the mesoporous structure, by drop casting a perovskite precursor solution on top of the carbon electrode.

In the above devices, a hole transport layer (HTL) is absent; thus, holes are transported through the perovskite layer to the carbon electrode. The absence of an expensive and unstable HTL, such as spiro-Ometad, and the lack of gold metal electrodes are among the advantages of this device architecture. Further advantages include good stability, preparation of devices using printable techniques under environmental conditions, and the relatively low cost [6, 11, 12]. On the other hand, their efficiency is lower than that of devices

FIGURE 1: Schematic structure of a carbon-based PSC using ZnO NW arrays as an electron transport layer (ETL).

with a HTL (<16% [3]); hence, certain issues have to be resolved to improve their performance and their competitive advantages which could lead to potential commercialization [3, 6, 8].

Of the different layers used in this architecture, the spacer layer plays an important role, namely, to prevent direct contact between the ETL and the carbon layer, acting as an insulator, and thus, its morphology is crucial. For example, there is an optimum thickness of the spacer layer in order to prepare high-efficiency devices [5, 13, 14], since the perovskite inside the pores of the spacer layer also absorbs part of the incoming light and the photogenerated electrons have to be transferred to ETL and holes to the carbon electrode, through the perovskite layer. Liu et al. [5] found that the efficiency was maximized when the thickness of the ZrO_2 layer was $1\ \mu\text{m}$.

Moreover, an uneven spacer layer would increase the probability of direct contact between ETL and carbon film. Liu et al. [15] prepared a flat and uniform spacer layer consisting of $\text{TiO}_2@\text{ZrO}_2$ core shell nanoparticles, achieving better insulating properties and a defect-free flat interface between carbon electrode and perovskite.

The properties of the spacer layer can also affect the morphology of the perovskite layer, since the latter is confined in the mesoporous spacer film. Meng et al. [4] used ZrO_2 and Al_2O_3 as spacer layers and found that the larger pores of the ZrO_2 layer are more favorable for the infiltration and crystallization of the perovskite, generating large grains, thus reducing the crystal boundaries.

Finally, a thick ZrO_2 layer can replace the mesoporous ETL, in an effort to simplify the manufacturing procedure, by reducing the number of layers and the number of annealing steps. Devices without the mesoporous ETL have showed efficiencies up to 9.7% [14]. On the other hand, in some cases, the ZrO_2 layer is absent. Then, to avoid a possible short circuit of the device, the growth of a compact and even perovskite film between the ETL and the carbon layer is necessary [15, 16], since otherwise undesirable internal losses could lead to low efficiency of the device.

In the current study, a double-layered film consisting of ZrO_2 nanoparticles and microparticles was used as a spacer layer for carbon-based PSCs. The light-scattering effect of ZrO_2 microparticles has been applied for the first time, as a method to enhance light fluence on the perovskite layer. In the presence of this layer, a fraction of light transmitted through the perovskite layer can be reflected back [17], thus

increasing the light fluence irradiating the perovskite. Reflection of light also takes place, when a gold electrode is used in other device architectures [6]. As a result, an efficiency improvement up to 30% was observed due to better light trapping from the double-layered ZrO_2 film, compared to a conventional spacer based on ZrO_2 nanoparticles. Finally, novel photodetectors having a simple structure of $\text{FTO}/\text{ZrO}_2/\text{perovskite}/\text{FTO}$ have been prepared, to explore simultaneously the light absorption ability and charge transport properties of the $\text{ZrO}_2/\text{perovskite}$ system.

2. Materials and Methods

2.1. Materials and Preparation of ZnO NW Arrays. ZnO NW arrays were grown on conductive glass substrates (FTO, $R_{\text{sh}} = 15\ \Omega/\text{sq}$, supplied by GreatCell Solar), using a method reported in our previous work [18]. First, the conductive side was patterned using zinc powder and HCl acid solution (20% v/v), to form two electrically isolated areas, and then, the substrates were cleaned using a standard procedure [18, 19]. After cleaning, a seed layer was prepared on the conductive side of the substrates by spin coating, using a solution containing 0.05 M zinc acetate dihydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, Merck, 98%) in absolute ethanol. Each time, five drops of the solution were spin coated at 1000 rpm for 30 s and the procedure was repeated five times. The films were subsequently annealed at 300°C for 120 min to achieve their decomposition to ZnO seed nanocrystals.

The seeded substrates were placed in an aqueous solution, with a total volume of 15 ml, containing 50 mM zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Merck, 98%), 25 mM hexamethylenetetramine ($\text{C}_6\text{H}_{12}\text{N}_4$, HMT, Merck), 0.45 M NH_4OH , and 0.03 g PEI (MW = 800). The seeded substrates were placed in the growth solution facing down and inserted in an oven at 88°C for 50 min. Finally, after growth, the substrates were rinsed with triple deionized (3D) water and annealed at 300°C for 2 h.

2.2. Materials and Preparation of ZrO_2 and Carbon Pastes. For the preparation of the ZrO_2 pastes, either a commercial ZrO_2 nanopowder (0.8 g) with particle diameter $d = 15\text{--}25\ \text{nm}$ (99%, Alfa Aesar) or a ZrO_2 powder (0.8 g) consisting of microparticles (99.7%, Cerac Z-1074) was ground in a porcelain mortar initially with a small volume of 3D water (0.5 ml), while afterwards ethanol (5 ml) was added dropwise under continuous grinding for at least 15 min. The paste prepared in that way was transferred to a beaker by adding 20 ml of ethanol and stirred at $90\text{--}100^\circ\text{C}$, until nearly complete evaporation of ethanol and water was achieved. Finally, 3 g of a 10 wt% ethyl cellulose solution in EtOH (Sigma-Aldrich, viscosity 22 cP), acting as a binder, and 2 g α -terpineol (Sigma-Aldrich, analytical standard) were added, followed again by stirring at $90\text{--}100^\circ\text{C}$ to achieve the desired viscosity of the paste.

A similar method was used for the preparation of the carbon paste, where 0.4 g of graphite powder (99%, $7\text{--}11\ \mu\text{m}$, Alfa Aesar), 0.25 g carbon black (Vulcan XC-72), and 0.05 g ZrO_2 nanopowder were ground in a porcelain mortar with 1 ml of 3D water and 3 ml of ethanol. After transferring to a

beaker by adding 30 ml of ethanol and stirring at 90–100°C, ethyl cellulose (3 g, 10 wt% in EtOH) and α -terpineol (2 g) were added, followed again by stirring at 90–100°C to achieve the desired viscosity of the paste.

2.3. Fabrication of the Devices. A ZrO_2 film (N_ZrO_2) was deposited on the grown ZnO NW arrays, via the doctor blade method, using the paste with the zirconia nanoparticles. The films were annealed at 400°C for 1 h. After cooling at room temperature, deposition of the carbon paste followed, ensuring that the carbon film was attached to the side of the patterned substrate serving as cathode (Figure 1). Finally, the films were annealed at 400°C for 30 min, in order to thermally decompose the organic ingredients used for the preparation of the carbon paste, since the as-prepared carbon films were nonconductive. For the preparation of the double-layered ZrO_2 film (DL_ZrO_2), on the surface of N_ZrO_2 film, a second layer was deposited with the doctor blade method, using the ZrO_2 paste with the microparticles. After annealing at 400°C for 30 min, a carbon film was deposited to complete the devices.

A small amount (10 μl) of a perovskite precursor solution (1.3 M methylammonium iodide and 1.3 M lead iodide in γ -GBL) was added dropwise on top of the carbon film (Figure 1). The perovskite solution was infiltrated through the porous network of the films, and the samples were annealed at 80°C for 30 min to achieve crystallization of the perovskite.

2.4. Characterization Methods. The morphologies of the films were evaluated using field emission scanning electron microscope (FE-SEM) (FEI Inspect TM F50). The crystal structures were investigated using X-ray diffraction (XRD) (Bruker D8 diffractometer), operating at 40 kV and 40 mA, employing Cu K α radiation ($\lambda = 1.54056 \text{ \AA}$). The thickness and the roughness (R_a) of the films were measured by an Ambios XP-1 stylus profilometer, while a UV-Vis spectrophotometer (Hitachi, U-3010) was used for measuring the absorbance of the films at normal incidence.

The J - V curves of the prepared solar cells were recorded with the use of an Oriel 96000 solar simulator, equipped with an AM1.5G filter, in conjunction with a Keithley 236 source meter. The incident irradiance was fixed at 1000 W/m^2 [19, 20]. The J - V and the transient photocurrent curves of the prepared photodetectors were recorded using a LED lamp (warm white, 30 W) and a potentiostat (Princeton Applied Research, Model 263A). The incidence irradiance in this case was fixed at 7.5 mW/cm^2 , as measured by a thermal power sensor (S322C, Thorlabs) using a PM100D power console.

3. Results and Discussion

3.1. Film Morphology. The morphologies of the different films are illustrated in Figure 2, starting from the ZnO NW arrays (Figure 2(a)), the carbon film (Figure 2(b)), and the ZrO_2 films (Figures 2(c) and 2(d)), prepared using the microparticles (MPs) or the nanoparticles (NPs), respectively. The average diameter and the length of the NWs are

$55 \pm 10 \text{ nm}$ and $0.8 \pm 0.2 \mu\text{m}$, respectively. Similarly, the average thickness of the carbon films is $25 \pm 3 \mu\text{m}$, comprised of nanoparticles with size 60–70 nm. The differences between the two ZrO_2 films are noticeable. A rough morphology and particles with size ranging from 0.5 to $2.0 \mu\text{m}$ (Figure S1) appear for the ZrO_2 film with the microparticles, while a more even morphology appears for the ZrO_2 film with the nanoparticles.

The crystal structure of the ZrO_2 films has been examined by XRD. Figure 3(a) presents the diffraction pattern for the films prepared using ZrO_2 microparticles (MPs) or nanoparticles (NPs), deposited on a glass substrate. For both films, the main diffraction peaks appear at 28.5° and at 31.8° , assigned to crystal planes (-111) and (111), respectively, of monoclinic zirconia [21, 22]. In the case of the ZrO_2 microparticles, the peaks are sharper, indicating an increased crystallinity and that the film consists of larger crystallites (Figure 3(b)). According to the Scherrer equation [19, 21], the size of the crystallites is 19.5 nm and 20.8 nm or 41.2 nm and 40.5 nm, if the FWHM of diffraction peak at $2\theta = 28.5^\circ$ or at $2\theta = 31.8^\circ$ is used for the calculations, in the case of ZrO_2 -NPs and ZrO_2 -MPs, respectively (Figure 3(b)). Moreover, the position of the other peaks and their number are the same for both films, showing the similar crystal structure.

3.2. Morphology of the Perovskite Layer Deposited on the Surface of ZrO_2 Films. The morphology of the perovskite layers, deposited on the surface of a double-layered ZrO_2 film (DL_ZrO_2) and on the surface of a normal ZrO_2 film (N_ZrO_2), is illustrated in Figures 4(a) and 4(b), respectively. In both cases, most grains of $\text{CH}_3\text{NH}_3\text{PbI}_3$ have size less than $50 \mu\text{m}$ (Figures 4(c) and 4(d)). Nevertheless, in the case of the DL_ZrO_2 film, larger grains with size exceeding $100 \mu\text{m}$ are evident in contrast to the N_ZrO_2 film. Larger-sized perovskite crystals favor charge transport, due to the presence of fewer grain boundaries [23, 24]. The surface of the DL_ZrO_2 film consists of ZrO_2 microparticles, with large gaps between them. As a result, the free space between them is filled initially with the perovskite solution and permits the growth of large grains of $\text{CH}_3\text{NH}_3\text{PbI}_3$. The grainy morphology of the perovskite layer is a characteristic of the method used for its preparation, using a one-step deposition method from a precursor solution of PbI_2 and $\text{CH}_3\text{NH}_3\text{I}$ in γ -GBL [5, 24, 25].

The crystal structures of the perovskite layers after deposition on the surface of the two different ZrO_2 films are illustrated in Figure 5 and Figure S2 (closer view). The peaks at 13.98° , 14.1° , 20° , 23.5° , 28.2° , 31.5° , 40.5° , and 43.1° are assigned to (002), (110), (112), (211), (004), (114), (224), and (314) crystal planes of $\text{CH}_3\text{NH}_3\text{PbI}_3$, respectively [26, 27], showing a perovskite layer with a tetragonal crystal structure. No peaks assigned to PbI_2 are observed [28], showing the efficient formation of the perovskite by the one-step method. The only difference observed is that the main peaks in the case of N_ZrO_2 film are (002), (110), and (211), while in the case of the DL_ZrO_2 film, the main peaks are (110), (004), and (114), revealing a difference in the crystal orientation.

FIGURE 2: SEM images of (a) ZnO NW arrays, (b) carbon film, (c) ZrO₂ film using microparticles, and (d) ZrO₂ film using nanoparticles.

FIGURE 3: (a) XRD pattern of the two different ZrO₂ films deposited on glass. (b) Magnification of the two main diffraction peaks.

3.3. Optical Properties. The UV-Vis absorption spectra of the N_ZrO₂ and DL_ZrO₂ films deposited on glass (Figure 6(a)) reveal an increased absorbance, covering all the visible and the near-infrared region, from 400 nm to 800 nm, in the second case. The average film thickness and roughness (R_a) are 2.1 μm and 0.54 μm for the N_ZrO₂ and 2.7 μm and 0.64 μm for the DL_ZrO₂ film (Figure 6(b)). As a result, the thickness of the scattering layer consisting of ZrO₂ MPs is only 600 nm.

The increased absorbance for the DL_ZrO₂ film is ascribed to the higher scattering ability owing to the size of

the particles. Indeed, particles with an average size comparable with the wavelength of light are more efficient scatterers [29]. The presence of the large ZrO₂ particles in the double-layered spacer film results in an increase of the optical path length, due to the improved scattering efficiency [17, 30–32]. Moreover, scattering of light is more intense as the wavelength of light decreases, as expected from Rayleigh and Mie scattering theory. Finally, in the case of the double-layered spacer film, the absorbance is nearly steady from 800 nm to 400 nm.

FIGURE 4: SEM images of (a) the perovskite layer deposited on the surface of a DL_ZrO₂ film (inset: SEM image from a different area) and (b) on the surface of a N_ZrO₂ film (80°C/1 h). (c) Distribution of grain size in the case of a DL_ZrO₂ film and (d) distribution of grain size of a N_ZrO₂ film.

FIGURE 5: XRD pattern of the perovskite layer deposited on the surface of the two different ZrO₂ layers.

3.4. Performance of Photodetectors. To evaluate the absorption ability and the charge carrier mobility of the perovskite layer in the presence of the two different ZrO₂ layers, independently from the development of carbon-based PSCs, photodetectors having the structure FTO/ZrO₂/perovskite/FTO (Figure 7) were prepared. In this configuration, the ZrO₂ layer serves as a scaffold for the deposition of the perovskite. Both light absorption and charge transport take place only through the perovskite layer, since electron transport from the perovskite to the ZrO₂ is inhibited due to the positions of the energy bands [33].

Figure 7 illustrates the *J-V* curves of ZrO₂/perovskite photodetectors under illumination, using a LED lamp with an intensity of 7.5 mW/cm². The linear response of the photocurrent in response to the applied bias potential indicates the formation of ohmic contacts between the perovskite and the FTO electrodes (Figure 7(a)). The distance between the two electrodes is 1.8 cm, far from being optimized, since the distance between the electrodes is usually few tens of μm [34–36]. Nevertheless, the photocurrent density produced at a bias potential of 1 V (Figure 7(b)) in the case of the DL_ZrO₂ film is nearly 325 nA/cm², almost 35% larger than the photocurrent density produced in the case of the N_ZrO₂ (240 nA/cm²). As a result, the responsivity of the

FIGURE 6: (a) UV-Vis absorbance spectra of N_ZrO₂ and a DL_ZrO₂ films, deposited on glass, and (b) film thickness of the corresponding films.

FIGURE 7: (a) Current density-voltage curves of photodetectors and (b) transient photocurrent response during on-off illumination at a bias potential of 1 V.

DL_ZrO₂/perovskite photodetector is 0.043 mA/W, compared to 0.032 mA/W in the case of the N_ZrO₂/perovskite photodetector [34]. Figure 7(b) shows five consecutive light on (20 s)/light off (30 s) cycles, observing in both cases that the response is very fast and the obtained photocurrent values are highly reproducible. The rise time for both photodetectors was 98 ms, while the fall time was 129 ms and 133 ms in the case of DL_ZrO₂ and N_ZrO₂, respectively (Figure S3).

The apparent low value of responsivity is attributed to two main reasons: the long distance between the electrodes (L), since the responsivity is inversely proportional to L^2 [36], and the unfavorable position of the FTO bands for hole extraction. Despite the current simple nonoptimized device

structure, a comparison between the two different ZrO₂ layers can be made. The increased photocurrent in the case of the DL_ZrO₂ film can be explained by the increased light absorption of the perovskite layer, due to the efficient back-scattering of light by the ZrO₂ microparticles. The charge transport ability through the perovskite layer remains the same, as indicated by the similar responses to on/off cycles and the similar values of the rise and fall times. Finally, the presence of different dominant crystal planes of the perovskite (Figure 5) seems to bear no influence on the charge transport ability.

3.5. Performance of Photovoltaic Devices. The effect of the thickness of the spacer layer on the efficiency of carbon-

TABLE 1: Characteristic photovoltaic properties of carbon-based PSCs prepared with the two different spacer layers, having different thicknesses.

Spacer	Thickness (μm)	Roughness R_a (nm)	V_{oc} (V)	J_{sc} (mA/cm^2)	FF	η (%)	R_s ($\Omega \text{ cm}^2$)
N_ZrO ₂	2.5 $\pm$ 0.4	520 $\pm$ 25	0.59 $\pm$ 0.07	10.9 $\pm$ 0.4	0.41 $\pm$ 0.04	2.2 $\pm$ 0.4	19 $\pm$ 1
	4.6 $\pm$ 0.6	575 $\pm$ 25	0.68	3.3 $\pm$ 0.7	0.47 $\pm$ 0.05	1.2 $\pm$ 0.2	34 $\pm$ 2
	8.7 $\pm$ 0.9	620 $\pm$ 100	0.68 $\pm$ 0.06	2.0 $\pm$ 0.9	0.44 $\pm$ 0.04	0.4 $\pm$ 0.2	53 $\pm$ 9
DL_ZrO ₂	2.6 $\pm$ 0.2	630 $\pm$ 30	0.67 $\pm$ 0.01	14 $\pm$ 2	0.31 $\pm$ 0.02	2.9 $\pm$ 0.4	29 $\pm$ 5
	3.8 $\pm$ 0.2	660 $\pm$ 70	0.60 $\pm$ 0.08	11.8 $\pm$ 0.7	0.30 $\pm$ 0.02	2.2 $\pm$ 0.6	30 $\pm$ 5
	8.3 $\pm$ 0.1	1170 $\pm$ 45	0.63 $\pm$ 0.05	5 $\pm$ 2	0.32 $\pm$ 0.06	1.0 $\pm$ 0.3	62 $\pm$ 5

based PSCs was examined first. As has been reported elsewhere [5, 13, 14], the increase of the spacer layer thickness causes drastic decrease of the device efficiency. Indeed, the current data confirm that increasing the thickness of the zirconia NP layer (N_ZrO₂) from 2.5 to 9 μm (Table 1) causes decrease of the efficiency from 2.2 to 0.4%, due to the reduction in current density (Figure 8(a)). A thicker zirconia layer provides better insulating properties (Figure S4), since the contact between the carbon layer and the ZnO NWs was minimized, preventing recombination of carriers at the interface. As a result, a slight increase in the open-circuit potential is observed [5, 13], but on the other hand, diffusion of carriers to the carbon electrode becomes impeded and recombination is more likely in bulk, thus limiting the photocurrent and hence the overall efficiency (Figure 8(a), inset), while FF is nearly insensitive to film thickness.

When a double-layered ZrO₂ film was used as a spacer (DL_ZrO₂), the efficiency was increased in all cases (Figure 8(b)), due to the enhancement in the photocurrent density, even though the value of FF was inferior compared to that of the N_ZrO₂ film (Table 1). For example, using a double-layered ZrO₂ film 2.5 μm thick, the efficiency increased by nearly 30% compared to the N_ZrO₂. The improvement can be explained by the enhanced light-scattering ability of the double-layered film, as shown in Figure 6, and the improved responsivity of the photodetectors in Figure 7, resulting in higher absorption of light by the perovskite layer and thus higher photocurrent density. The thickness of the scattering layer was 0.5 $\pm$ 0.2 μm , in all cases.

To improve further the efficiency of the devices, modifications were made in the device construction by reducing the width of the etched area of the substrate (Figure 1), from 5 mm to few μm [37], whereas the amount of the perovskite precursor solution was reduced from 10 to 5 μl . To achieve crystallization of the perovskite, the samples were annealed in this case at 60°C for 1 h. Figure 9 displays the characteristic J - V curves of the improved devices, having the two different configurations of the ZrO₂ layers (N_ZrO₂ and DL_ZrO₂), with an average thickness of 2-2.5 μm . The results are consistent with previous findings, and the efficiency of the devices is comparable to that of the devices having a similar structure in the literature (Table S1). For example, Wang et al. in [38] have measured an efficiency

of 5.5% for carbon-based PSCs, having ZnO nanorod arrays as an electron transport layer (ETL), while in [39], the maximum efficiency achieved was 3.6%. Higher efficiencies have been achieved only in the case where a hole transport medium and a metal electrode have been used (see Table S1 for a comparison of relevant data).

The roughness of the films increases owing to two reasons: (i) due to the thickness increase of the ZrO₂ films and (ii) because of the presence of the second layer, consisting of ZrO₂ microparticles (Table 1). A rough spacer surface hampers the formation of a good interface between the perovskite and the carbon film. Formation of voids due to incomplete filling with the perovskite cannot be excluded, even though a perovskite layer with larger grains can be formed (Figure 4). Thus, the nonideal interface results in an increased series resistance (R_s) of the devices (Table 1) and in a lower charge transfer rate at the interface perovskite/carbon [16]. Both factors contribute to the reduced FF of the devices with the DL_ZrO₂ film. R_s was derived from the linear fitting using equation (1) and more specifically from the intercept with the y -axis (Figure 10) [40]:

$$-\frac{dV}{dJ} = \frac{Ak_B T}{e} \cdot (J_{sc} - J)^{-1} + R_s. \quad (1)$$

A is the ideality factor of the diode, k_B is the Boltzmann constant, T is the absolute temperature, e is the elementary charge, and R_s represents the series resistance. The above equation is derived from the I - V characteristic of a solar cell, using a one diode model, and holds with the approximation that the shunt or parallel resistance of the solar cell (R_{sh} or R_p) is very large compared to the series resistance (R_s).

As regards the low efficiency of the devices in the present study, a number of reasons can be invoked: first, no additives such as 5-ammoniumvaleric acid (5-AVA) were used in the perovskite precursor solution. With this additive, better pore filling and modification of the ETL/perovskite interface can be achieved [41]. Furthermore, the surface of ZnO NWs has not been modified in order to suppress charge recombination, as in [38], where ZnO/TiO₂ core shell nanorods were applied in carbon-based PSCs and a two-deposition method was used for the formation of the perovskite layer. Nevertheless, the current study is intended to demonstrate that simple low-cost methods can be employed to prepare devices

FIGURE 8: Typical J - V curves of PSCs prepared with different spacer thicknesses of (a) N_ZrO_2 films and (b) DL_ZrO_2 films. Inset graphs: efficiency variation with ZrO_2 film thickness and in parentheses number of devices used for calculation of the error bars.

FIGURE 9: J - V curves of improved PSCs prepared with a N_ZrO_2 film (a) and a DL_ZrO_2 film (b), as a spacer.

(photodetectors and solar cells) with realistic efficiencies, since the current literature has revealed that the cost and complexity in device preparation are not always commensurate with the increase of efficiency.

4. Conclusions

In summary, we have proposed and demonstrated the use of double-layered ZrO_2 films, one layer consisting

of ZrO_2 nanoparticles and the other one of ZrO_2 micro-particles, acting as spacers in carbon-based PSCs. With this architecture, beyond its common role as an insulator, the ZrO_2 film obtains a new role, i.e., that of a light scatterer for more efficient light harvesting by the perovskite layer.

The surface morphology of the double-layered ZrO_2 films affects the growth of the perovskite crystals. Larger grains with different dominant crystal planes were grown, since the presence of large-sized ZrO_2 particles ensures the availability of free space for perovskite crystal growth. Besides, the scattering ability is enhanced, improving light absorption of the perovskite layer, without affecting its charge transport ability, as observed by measuring the responsivity and the rise and fall times of photodetectors, based on a ZrO_2 /perovskite system.

The presence of a double-layered ZrO_2 film as a spacer layer in carbon-based PSCs resulted in an increased photocurrent density, due to the better light-harvesting efficiency. The observed changes depend on the ZrO_2 film thickness and the surface roughness. The increased surface roughness of the double-layered ZrO_2 films prevents the formation of a smooth interface between the ZrO_2 and the carbon layer, resulting in an increased series resistance of the devices and a lower FF , compared to devices having a conventional spacer layer. However, the overall effect of the DL_ZrO_2 film in the efficiency of the resulting devices is certainly positive, as an increase in the efficiency reaching up to 30% is observed. The present work provides evidence that the ZrO_2 film used in carbon-based PSCs can affect significantly the device performance, not only acting as a simple insulator layer but as a light scatterer as well.

FIGURE 10: Typical plots of $-dV/dJ$ vs. $(J_{sc} - J)^{-1}$ of PSCs, having (a) a N_ZrO₂ film as a spacer with different thicknesses and (b) a DL_ZrO₂ film as a spacer with different thicknesses.

Data Availability

The (SEM images, graphs) data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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Supplementary Materials

Figure S1: grain size distribution of a ZrO₂ film using a ZrO₂ powder consisting of microparticles (Cerac Z-1074). Figure S2: XRD pattern of the perovskite layer deposited on the surface of the two different ZrO₂ layers. Figure S3: transient photocurrent response during on-off illumination at a bias potential of 1 V. Figure S4: typical J - V curves prepared with a N_ZrO₂ film as a spacer with different thicknesses, before the deposition of the perovskite. Table S1: materials and efficiency of perovskite solar cells based on ZnO as ETL. (Supplementary Materials)

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