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Bragg gratings nanostructuring of TiO_2 layer in dye sensitized solar cells: an efficient method to enhance light harvesting

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In this paper, we report an experimental procedure for active layer nanostructuring in Dye Sensitized Solar Cells (DSCs) to enhance light harvesting. A Bragg grating has been realized on a high performance commercial photoresist by means of Laser Interference Lithography (LIL) technique. Subsequently this structure has been replicated by a Soft Lithographic process on a Polydimethylsiloxane (PDMS) mold, which finally allowed the direct imprinting of the DSC's titania layer under UV illumination. Morphological analysis demonstrated a successful pattern transfer over a large area. Spectroscopic and photovoltaic measurements have been performed on nanostructured and traditional bare DSC. In the spectral range 500-750 nm the patterned cell showed a lower transmission and reflection indicating that the grating acts efficiently as a light harvesting element. I-V and Incident Photon to Current Efficiency (IPCE) characterizations showed an enhancement of 31% of the cell efficiency, confirming the effectiveness of this method.

Introduction

Dye Sensitized Solar Cells (DSCs)[1] are a very attractive and economically valuable alternative to silicon based photovoltaic devices. In DSCs light is absorbed by sensitizers, usually dye molecules, having a broad-band absorption within solar spectrum range. The dye is anchored to the surface of a wide bandgap semiconductor (typically mesoporous TiO_2) in contact with a liquid electrolyte, therefore DSCs are categorized as photo-electrochemical devices. All the mentioned components are enclosed between two transparent conducting glasses, generally Fluorine doped Tin Oxide (FTO). The exposure of a DSC to solar light through the upper electrode results into the photoexcitation of the dye, followed by the injection of electrons into the conduction band of the oxide. The electrons then can reach the bottom photoelectrode, giving rise to an electrical signal. The ground state of the dye molecules is then restored by electron donation from the electrolyte, generally the redox couple I^-/I^{3-}, while on the counter-electrode, a thin platinum layer acts as a catalyst for the electrolyte restoring.

Since their discovery in 1991 by Grätzel and O'Regan[2], the optimization of the conversion efficiency[3] has represented the main challenge of this technology and nowadays has reached a value of 12.3%[4]. First attempts to improve DSCs performances concerned component modification with respect to the originally proposed cell, like the research of new semiconductors as electron acceptors[5], more stable dyes[6-9] or dye blends[10] able to match a major portion of the solar spectrum and new electrolyte species for a better ionic conductivity[11-13]. In addition to these improvements also photon management can be pursued in order to increase the conversion efficiency. Indeed, only a part of the incident photons are absorbed by the sensitizers since a fraction is transmitted outside or it is partially absorbed by the electrolyte, both these mechanisms resulting in a decrease of the efficiency. To avoid or reduce these processes different strategies have been

proposed which are mostly based on the introduction of optical elements into the cell architecture, able to lengthen the photon path through the active layer. In this way a better radiation-matter interaction is achieved resulting into an increased photon absorption probability, an increased DSC's light harvesting efficiency (LHE) and consequently a higher photogenerated current. The first successful LHE approach regarded the introduction of scattering layers[14]. The idea behind is that incident photons, not absorbed by the dye molecules, are reflected back into the active layer by means of a polydisperse distribution of TiO_2 nanospheres. The effect of a mixture of disordered and differently sized particles produces a relevant absorption enhancement[15]. However, such type of cells appear completely opaque, making them not suitable for several applications like for instance architectural integration (Building Integrated Photo-Voltaic, BIPV).

To overcome this disadvantage new configurations exploiting periodic nanostructures within the cell such as photonic crystals have been developed.[16-18] In this case an efficient light trapping is achieved for well-defined spectral ranges preserving at the same time the overall cells transparency.

Other examples of photonic management include the introduction of optic elements on the photoanode surface[19-21], the insertion of nanostructured elements such as nanowires[22], nanotubes[23,24] or nanorods[25-27] inside DSCs architecture or on its backside[28].

Recently a theoretical work[29] predicted that the introduction of a Bragg grating having 300 nm height and 500 nm pitch placed at the interface between the titania layer and the electrolyte, for a squaraine-dye based cell, would produce an increase in the absorption of 23.4% compared to a standard DSC.

In this work, we report the experimental evidence of the light management effectiveness of the Bragg grating effect on a DSC. A simple, efficient and low-cost procedure for titania layer nanostructuring has been developed. First, we fabricated periodic Bragg gratings on a high performance commercial photoresist by means of Laser Interference Lithography (LIL) technique. Then we used the fabricated structures as masters to replicate the pattern on soft Polydimethylsiloxane (PDMS) molds. The obtained molds were used to directly imprint DSC titania layers by Soft Lithography (SL) exploiting UV illumination. Morphological characterization of both master and structured titania layers was performed by Atomic Force Microscopy (AFM) and Scanning Electron Microcopy (SEM). The replicated structures showed the same morphological features with respect to the original masters. Layers have been consistently nanostructured over a large area with good quality. A set of DSCs has been fabricated using the structured titania layers realized FTO electrodes and their conversion efficiency has been compared to traditional bare ones fabricated in the same experimental conditions, in order to obtain the most representative comparison.

The properties of the nanostructured and plain cells have been compared. Spectroscopic measurements showed a decrease of the transmitted and reflected light in the spectral range of interest (500-750 nm) for the patterned cells suggesting an improvement in light harvesting by the gratings. I-V measurements show a higher short-circuit photocurrent of 15%, which resulted in an enhancement of the cell conversion efficiency equal to 31%.

Experimental Section

From master fabrication to titania nanoimprinting

The procedure has been described in details in previous papers[30-32]. In order to produce the master with the periodic Bragg gratings by means of LIL technique we chose a high performance photoresist (Clariant AZ 5214E). Photoresist was spin coated on a 2.5 × 2.5 cm^2 Corning glass substrate with a speed of 3000 rpm for 30 seconds. It resulted in a film of 1.5 μm thickness. The sample was pre-baked on a hot plate at 95 °C for 5 min to remove the solvent. This determines a slight densification of the photoresist. Then it was exposed to the 364 nm line of an Ar^+ laser with power density of 34 mW/cm^2 for 4 seconds in a Lloyd mirror set-up. Thanks to this configuration interference fringes are produced on the film surface. The interference pattern produces a succession of exposed and unexposed regions on the resist. The sample is mounted on a rotational stage to permit the adjustment of the grating's periodicity by setting the incident angle of the beam according to the Bragg law: $2\Lambda sin\theta = n\lambda$, where n is an integer, λ is the wavelength of the incident radiation, Λ is the grating pitch and θ is the angle of incidence. The subsequent immersion of the sample into the specific developer bath results in the easy removal of the unexposed -not polymerized- areas of the film. Both UV light exposition and development time are strongly related to structure's height and profile shape and have been carefully optimized. The final step was a post-bake treatment at 120 °C for 1 min in order to stabilize the photo-polymerized structures which will act as masters in the following.

Masters were replicated with SL technique exploiting a PDMS elastomer. PDMS solution was prepared mixing Sylgard 184 (Dow Corning) and its initiator in 10:1 volume ratio. The liquid precursor obtained was poured onto the master and held under vacuum pumping for 30 minutes to remove air bubbles. Then it was cured at 75 °C for 1 hour and peeled off from the master. The final solid PDMS mold was used to replicate the Bragg structures on the titania layer by UV nanoimprinting technique. The obtained molds offers a great advantage since they can be re-used to produce the same structures several times without noticeable degradation[33].

A thin layer of a transparent commercial titania paste (18NR-T DyeSol), whose particles have an average diameter of 20 nm, was screen printed on a glass substrate having an FTO layer (8 Ω cm-2, Pilkington®) over a 0.25 cm^2 active area, and left at room temperature for few minutes in order to permit a partial evaporation of the solvent and titania particle relaxation. Such a delay is necessary to guarantee a good adhesion between mold and titania layer surface without sticking.

The mold was then placed on the titania layer with a slight and constant pressure over the entire area and subsequently the

system (PDMS/titania layer) has been irradiated with a 400 Watts Hg-Xe UV lamp for 10 minutes to imprint the layer. After this step, the PDMS mold was peeled off from the titania layer and the latter was heated at 80 °C for 40 minutes in order to stabilize the imprinted pattern.

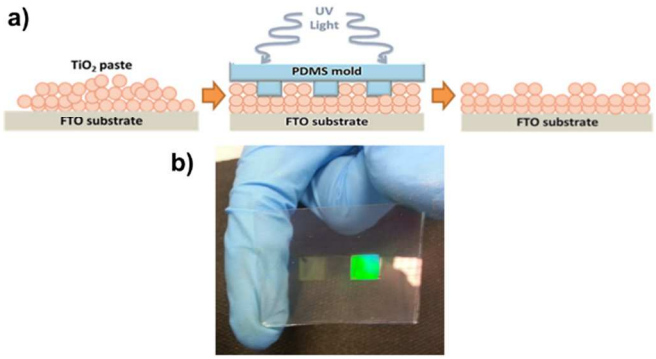

Fig.1. a) Nanoimprinting experimental steps. b) Final titania nanostructured layer (right side) compared to the bare one (left side). The bright coloration of the nanostructured layer is only due to the light diffraction effects.

The final step is a densification process where the temperature is ramped up to 500 °C within an hour to definitely calcine the structures. The layer thickness at the end of the process was approximately 3 µm. The whole procedure is schematically shown in Figure 1a). The final nanostructured titania layer is shown in Figure 1b) (right side of the glass substrate) together with the unstructured layer (left side). The intense coloration clearly visible in the picture is due to diffraction effects. The nanostructured and bare layers have been deposited on the same FTO substrate in order to operate in the same experimental conditions and obtain the best comparison between the two cases.

It must be underlined that the nanoimprinting procedure has been successfully performed on several samples in order to validate the obtained results.

Morphological characterization of masters and imprinted titania layers was performed using Atomic Force Microscopy (VEECO) in air and in tapping mode and Scanning Electron Microscopy (Leo Supra 35 SEM-FEG). Layer thicknesses have been measured by profilometer technique using a Veeco Dektak® 150 profiler.

DSC assembly and characterization

The bare and the nanostructured titania layers, deposited on the same FTO substrate and having the same average thickness, were immersed together into a squaraine dye based ethanol solution (SQ2, Solaronix ®) for 5 minutes. After the immersion, the substrates have been rinsed with pure ethanol and dried under a weak air flux. The choice of fabricating cell with low concentration of dye molecule is dictated by our goal. We want to ascertain the validity of insertion of a grating in the cell in order to increase the light harvesting and it is necessary that a consistent fraction of the light reaches the grating. For the same reason we limited the titania layer thickness to about 3 µm. The counter-electrodes were obtained with other FTO substrates where a colloidal Platinum paste (Chimet) was deposited and heated at 420 °C for 30 minutes. Counter-electrodes were coupled to the photosensible anodes to realize the cells. DSCs cells were sealed by means of a thermo-polymer resin (Surlyn 25, Solaronix®). To complete the cells, a commercial high performance electrolyte solution (HSE Dyesol®) was introduced under vacuum by means of two free channels previously designed on the resin foil. Finally, the channels were sealed with a thermoplastic polymer. It is important to underline that all the steps for the assembly of reference and grating based DSCs have been the same in order to minimize any possible and unwanted experimental differences. Transmittance and reflectance measurements were performed on both nanostrucured and standard cells by means of an UV-VIS Spectrophotometer Shimadzu 2550. The incident light hits normally the photoanodes of the two samples and the transmitted and reflected light were collected by an integrating sphere and investigated in a range between 500-750 nm. I-V characterization was performed by means of a solar simulator (Sun 2000, Abet Technologies - 100 mW cm-2 with AM 1.5 G filter) whereas Incident Photon to Current Efficiency (IPCE) set up consists of 150W Xe OF lamp Newport Model 70 612 coupled with a Cornerstone 130 monochromator 1/8 m and a Keithley 2400 source meter.

Results and Discussions

The capacity to spread light of different wavelengths into different angles (diffraction effect) is the main characteristic of a grating. The spectroscopic properties of this optic element can be derived from the grating equation, defined as:

$$d(\sin\theta_i + \sin\theta_m) = m\lambda$$

where θ_i is the angle of incidence; θ_m the diffraction angle; m the order of the diffracted beam and d the periodicity of the structures (pitch). Grating acts as a dispersive optical component with several advantages with respect to a prism: being a planar device, it can be easily integrated in a cell and its angular dispersion can be tuned by varying the periodicity. The introduction of such element within a DSC device, in accordance with photon management strategies, can allow an increase of the average path of the photons in the active layer. Therefore, the number of dye molecules intercepted along the photon path should increase and the absorption and the photovoltaic properties enhanced consequently. To verify such hypothesis we realized nanostructured DSCs. A scheme of the cell is reported in Figure 2. In Figure 3 there are reported two 5×5 μm^2 3D AFM micrographs. Figure 3a) shows a master fabricated on AZ5214E photoresist and Figure 3b) the corresponding imprinted titania layer. The Bragg grating of the master presents a sinusoidal, well-defined profile (approximately 200 nm depth and 500 nm pitch). The imprinted titania layer which is composed by nanometric particles has a less defined profile due to superficial roughness. It presents an average height of 130 nm and a pitch of 500 nm. While the pitch of the replica is identical to the original master, the

grating height results slightly reduced of about 35% due to the molding process. SEM micrograph of the nanostructured titania layer is presented in Figure 4. A well defined and homogenous grating is clearly visible over a large area.

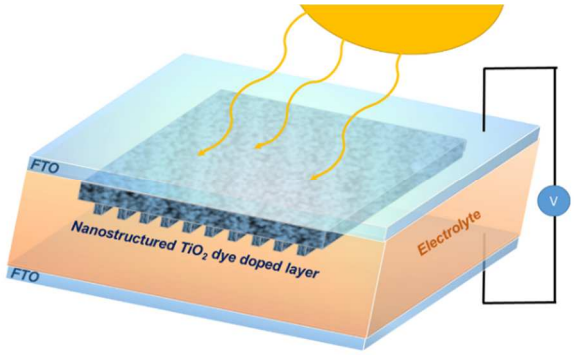

Fig.2. Schematic representation (not to scale) of the nanostructured DSC cell.

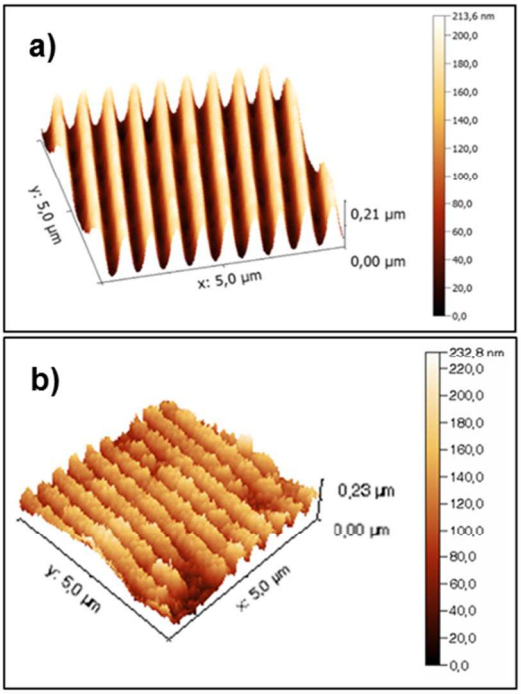

Fig. 3. a) 3D AFM micrograph of AZ5214 master layer and b) imprinted titania layer.

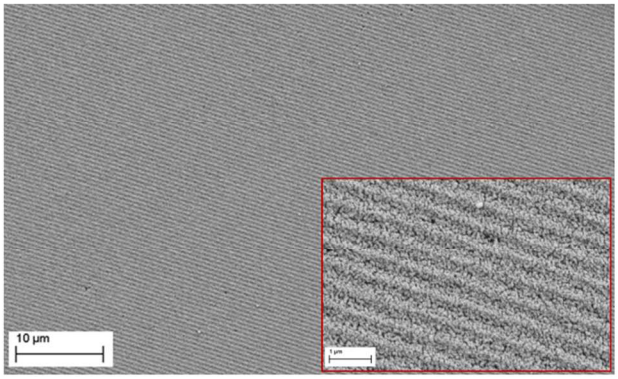

Fig. 4. SEM image of the nanostructured titania layer; a higher resolution image is reported in the inset.

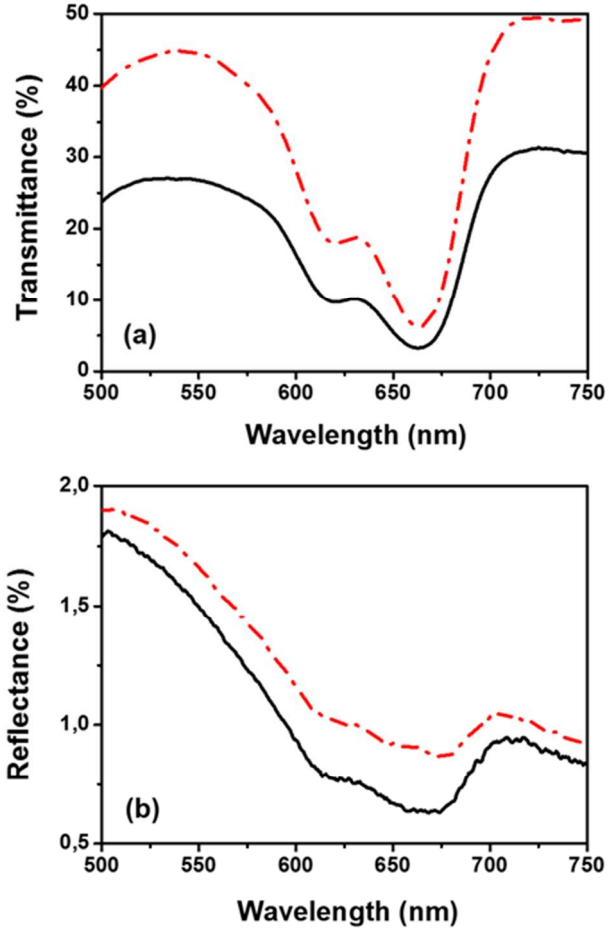

Fig. 5. Transmittance (a) and reflectance (b) spectra for the traditional bare cell (red dashed line) and the nanostructured cell (black solid line).

In Figure 5, the transmittance and reflection spectra (normal incidence) collected with an integrating sphere for the standard bare (red dashed line) and nanostructured (black solid line) cells are shown. An overall decrease in the transmission and reflection spectra for the patterned cell outlines the effect of the grating in the spectral range between 500 and 750 nm. When the incoming light strikes the grating it is diffracted both in the back and forward direction on the different diffraction orders thus producing such reduction. In particular it is the back-diffracted light which, having a longer path length in the active layer, interacts with a higher number of dye molecules and is absorbed more efficiently, giving rise to a lowering of the reflectivity and transmission. The process is schematically represented in Figure 6. This effect can be exploited to enhance the efficiency of the cell since the greater number of excited dye molecules can produce a higher number of photoelectrons.

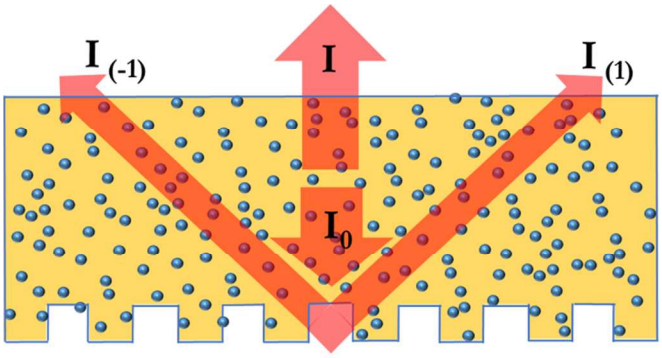

Fig. 6. Schematic representation of the phenomena involved when an incident light I_0 hits the grating structure within the cell. I represent the orthogonally reflected back light, while $I_{(1)}$ and $I_{(-1)}$ represent the first order of the diffracted back light. The diffraction paths involve an increased quantity of dye molecules (blue dots) affecting the transmission and reflection spectra.

In order to analyze if the spectroscopic behavior of the patterned cell has an influence on the photovoltaic properties, *I-V* characterization of both the bare and the patterned cells have been performed. A significant increment of 15% for short circuit photocurrent density (J_{SC}) and of 6% for open circuit photo-voltage (V_{OC}) was observed from the two characteristic curves (Figure 7 a)). The haracteristic cell parameters are summarized in Table 1. Incident Photon to Current Conversion Efficiency (IPCE) measurements have been performed. The results are showed in Figure 7b). By integrating the subtended areas of the two IPCE curves, in the spectral range of interest (500 - 750 nm) it was obtained a consistent enhancement equal to 31% for the nanostructured cell.

It has to be noticed that all the data reported have been obtained for a titania layer of thickness of about 3 µm and low dye loading since the cells have been immersed into the ethanol solution containing the SQ2 dye only for 5 minutes. This choice was dictated by the need to have a low absorption in the titania layer, otherwise the effect of the patterning would have been hidden. When the TiO_2 layer is heavily doped with the dye molecules or it is too thick, the incident light is completely absorbed by the upper part of the layer and cannot reach the underneath grating structure, preventing to verify the validity of the proposed method.

Comparing our experimental results with the simulated values recently obtained by Barettin et al.[29] we can make some considerations. In that work an increase of the absorption spectra of 23.4% in the spectral range 500-750 nm was estimated for a patterned cell with a 300 nm grating height and 500 nm pitch. In that case the absorption was calculated by an integration of the electromagnetic field in the titania layer taking into account also the diffracted beams induced by the grating. In our experimental measurements we report the transmission and reflectance spectra collected with an integrating sphere on a real cell where also the spectroscopic properties of the substrates and the electrolyte should be considered. Furthermore the morphological properties of our grating are not exactly the same as those reported in the theoretical work. For all these reasons a straightforward comparison cannot be accomplished. However, the reduction of the transmitted and reflected light in the same spectral range indicates that the grating effectively acts as a light harvesting element which was our main goal.

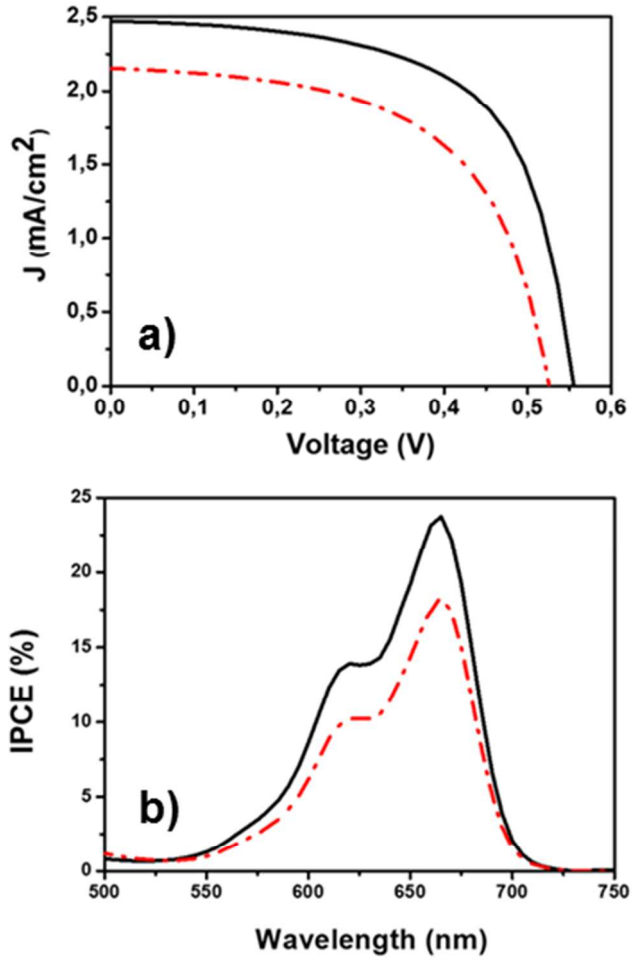

Fig. 7. a) *I-V* curves for the reference bare cell (red dashed line) and the nanostructured one (black solid line) under the same illumination conditions (100 mW/cm^2, AM 1.5G); b) IPCE comparison for the two samples.

	V_{oc} [V]	J_{sc} [mA/cm^2]	Fill factor [%]	Cell efficiency (η) [%]
Traditional cell	526×10^{-3}	2.15	57%	0.65%
Nanostructured cell	556×10^{-3}	2.47	62%	0.85%

Tab. 1. Comparison between reference and nanostructured cell parameters.

In addition to the scientific results illustrated above it is worthwhile to draw some considerations about the cells appearance. First of all, the semi-transparency of the cell is preserved as demonstrated by the transmission curves of Figure 5a). Moreover, depending on their angular orientation with respect to the incident light, we can see different coloration as showed in the photographs of Figure 8. These aspects are relevant for implementation of these devices for decorative applications and architectural purposes.

As a final remark, it is important to underline that the obtained results are very promising for future application even on different type of solar cells where the active layer is thin or not completely absorbing. The method shows great potentialities since it is easy to realize, has low cost and can be applied on large area by roll-to-roll technique.

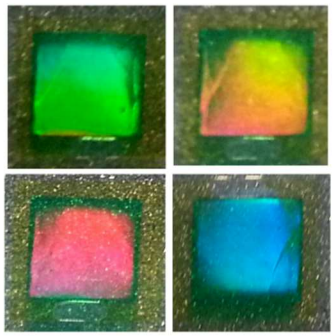

Fig. 8. Nanostructured solar cell pictures acquired changing the incident angle. Diffraction effects are clearly visible and give rise to an intense coloration.

Conclusions

In this work,we experimentally verified that the nanostructuting of the active layer of a DSC by means of low-cost Soft Lithography technique brings a consistent increase of the cell efficiency. We fabricated Bragg gratings on a high performance photoresist by means of Laser Interference Lithography obtaining structures whose dimensions are approximately 200 nm height and 500 nm pitch. We replicated the structures on a PDMS mold and used it to directly imprint a DSC titania layer by UV imprinting. Morphological characterization of the samples by means of AFM and SEM measurements showed the presence of good quality periodic structures on the titania layer over a large area. Nanostructured and standard DSCs have been fabricated under exactly the same experimental conditions in order to compare their photovoltaic response. A 31% increment of the efficiency for the nanostructured cells has been estimated by photovoltaic measurements. This result validates our previous theoretical calculations. The present work suggests that a cost effective and simple light management strategy based on soft lithographic method can be applied for DSCs efficiency improvement.

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Notes and references

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The patterned cell shows increased efficiency due to alternative light paths in the TiO_2 layer arising from diffraction effects.