

Luminescent Solar Concentrators: Boosted Optical Efficiency by Polymer Dielectric Mirrors

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ABSTRACT: We report on the optical efficiency enhancement of luminescent solar concentrators based on a push-pull fluorophore realized using high dielectric contrast polymer distributed Bragg reflectors as back mirrors. The Bragg stacks are obtained alternating layers of cellulose acetate to thin films of a new stable and solutionprocessable hydrated Titania-poly(vinyl alcohol) nanocomposite (HyTiPVA) with refractive index higher than 1.9 over a broad spectral range. The results gathered with these systems are compared with enhancements provided by standard Bragg reflectors made by commodity polymers. We demonstrate that the application of the Bragg stacks with photonic band-gap tuned to the low energy side of the dye emission spectrum induce a 10% enhancement of optical efficiency. This enhancement is the result of a performing photon recycling mechanism and is retained even on a scaled-up device where the Bragg mirrors are used in a mosaic configuration.

Introduction

Nowadays, cost reduction and efficiency enhancement are the driving forces for technological development of photovoltaic (PV) systems.¹ In recent years, luminescent solar concentrators (LSCs) became appealing thanks to light weight, high concentration factors, and to the possibility to operate with diffuse light without the need for expensive solar trackers and coolers.² Moreover, these devices can be easily integrated into modern buildings, also accordingly to the EU guideline 2010/31/UE, which, starting from 2020, will require each new building to be almost zero energy consumption.

Even though LSCs are potentially available for commercialization,³ some drawbacks are still limiting their massive commercial distribution. Such drawbacks include difficulties in the preparation of easily mountable modules and in the improvement of the device efficiency, which can be understood analyzing the LSC working principle. LSCs are highly transparent, planar and relatively thick waveguides doped with high quantum yield fluorophores.² The slabs have refractive index larger than the surrounding. In this way they favor total internal reflection of light emitted within the slab and its guiding to the sides of the slab, where standard solar cells are placed.² Notwithstanding their simplicity, several processes rule and limit their global efficiency (η_{dev}), including the usually poor matching between the fluorophore absorption spectrum and the solar emission (η_{ABS}) as well as the dye emission efficiency (η_{PL}). Beside the issues related to the fluorophore, the efficiency of the lateral solar cells (η_{PV}), of the waveguiding (η_{WG}), and of the trapping processes (η_{trap}) affect the entire energy generation process such that:

$$\eta_{dev} = \eta_{abs} \eta_{PL} \eta_{WG} \eta_{PV} \eta_{trap} \quad (1)$$

Concerning η_{abs} , several researchers focused on the development of new fluorophores with large spectral absorption and on tuning such absorption in the near infrared part of the solar spectrum, while maintaining the device transparency.^{2,4-6} To this end, high efficiency quantum dots synthesized without commonly used toxic heavy metals appear to be very promising.⁴ Conversely, if colored LSCs are chosen for aesthetic purposes, the efficiency can be increased by using smart near-infrared scatterers to funnel the non-absorbed long-wavelength solar radiation into the waveguide.^{7,8} Regarding η_{PL} , several dyes with quantum yield close to unity have been proposed.² On the other hand, self-absorption effects hinder η_{PL} , especially when large area devices and high fluorophore concentration are used. This drawback has been widely addressed engineering the fluorophore to maximize the Stokes shift. Moreover, Förster energy transfer has been investigated for molecular fluorophores, but the need to achieve proper blending on large area makes their use challenging.² To this end, donor-acceptor core-shell quantum dots are instead promising thanks to the possibility to couple different materials and achieve large Stokes shifts by simple wet chemistry.^{4,9,10} The use of fluorogenic dye exploiting

molecular aggregation or push-pull molecules could be an alternative approach to the problem.¹¹⁻¹⁴ Then, while molecular aspects, photoluminescence, and device efficiencies have been widely addressed and understood,^{2, 15, 16} many strategies are still under investigation for the enhancement of η_{trap} .¹⁷

In this work, we propose a new approach to enhance such parameter, while leaving the other efficiencies unchanged. For a waveguide with refractive index $n_{slab} \sim 1.5$ η_{trap} is evaluated as:

$$\eta_{trap} = \sqrt{1 - \left(\frac{n_{air}}{n_{slab}}\right)^2} \approx 0.74 \quad (2)$$

which means that almost 26% of photons emitted by the fluorophore leaves the slab within the escape cone and does not reach the lateral sides of the waveguide where the solar cells are placed (Figure 1). So far, the lost photons have been recycled using different reflectors including diffusive back reflectors, complex mirroring systems using plasmonic structures,¹⁷⁻²¹ rugate filters, or opal-like photonic crystals with photonic band gap (PBG) tuned on the emission spectrum.^{19, 22-24} More recently, the role of front- and back-reflectors on the performances of LSCs has been modelled²⁵ and applied to devices embedding micro-solar cells into the waveguide.²⁶

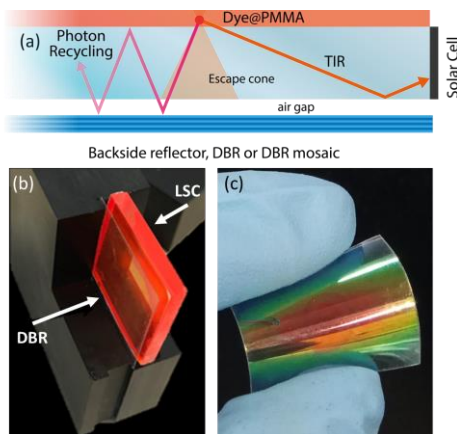


Figure 1. (a) Schematic of the LSC configuration and main processes involved. Digital photograph of (b) the LSC device coupled to a DBR and (c) of a flexible DBR.

In this work, we report on the role of polymer distributed Bragg reflectors (DBR) as back mirror - in place of a standard diffuser - on the performances of LSCs (Figure 1). Polymer DBRs and related structures with very high reflectance in a limited spectral region have been already exploited for lasing, fluorescence emission control, optical switches, and sensors.²⁷⁻³⁴ The DBR optical response, including the spectral position of the photonic band-gap, its reflectance intensity and bandwidth, are mainly dictated by the periodicity of the structure and the refractive index contrast among the polymer components.³⁴ Here, in order to increase the reflection bandwidth, we spun-cast high dielectric contrast polymer DBRs properly tuned to enhance the LSC performances. The DBRs allowed a ~10% enhancement of the optical efficiency, that is retained also on scaled-up devices through mosaicking of the DBRs. To this end, we employed both commodity polymers DBRs fabricated alternating cellulose acetate (CA), and poly (N-vinyl carbazole) (PVK) layers - sample series P - or CA and the novel processable very high refractive index hydrated titania: poly(vinyl alcohol) nanocomposites (HyTiPVA) (sample series H).

Results and discussion

The standard LSC devices were fabricated casting a thin layer of poly(methyl methacrylate) (PMMA) doped with a SilaFluo fluorophore on a glass slab. Then, a diffuser layer was applied to the back of the slab with an air gap (Figure 1, see Supporting Information S1 for the optical characterization of the diffuser and of the slab). As mentioned before, the air gap guarantees to maintain the slab guiding properties. This system represents the reference LSC. In our improved LSC devices, the diffuser was replaced with different Bragg stacks maintaining the air gap, as described in the Methods section.

The fluorophore used in this work is a red-emitting 2-amino-7-acceptor-9-silafluorene, where the amino group is $-N(CH_3)_2$ the donor, and the acceptor is $-CH]C(CN)_2$ (SilaFluo, Figure 2a). This dye shows fluorescence quantum yield of 65% and has been already successfully used in high performance LSCs.¹⁵ Figure 2b shows the absorbance and fluorescence spectra of the 1.5 wt.% dye embedded in the PMMA film and compares them with the transmittance spectrum normalized to a bare PMMA film. Notwithstanding the absorbance of SilaFluo overlaps the solar emission spectrum only partially, limiting η_{ABS} , it shows a relatively large Stokes shift. Indeed, while the absorption peak is positioned at 478 nm, the fluorescence is centered at 620 nm, limiting re-absorption losses which commonly affect η_{PL} . Moreover, SilaFluo is stable under LSC working conditions and provides an excellent matching with the spectral response of the side Si-solar cells.

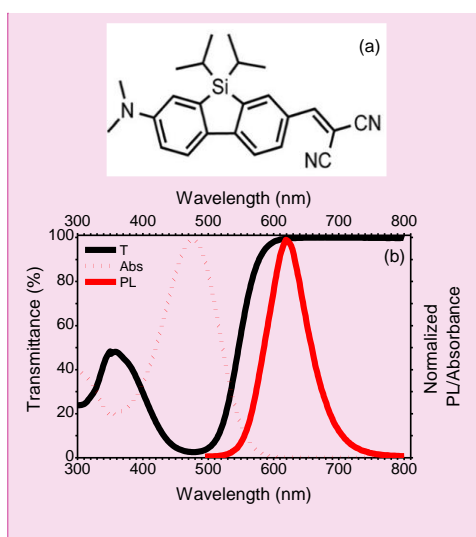


Figure 2. (a) Silafluor chemical structure. (b) Normalized transmittance, absorbance and photoluminescence spectra of the 1.5 wt.% Silafluor-PMMA film.

Two series of DBRs were fabricated with the CA:PVK and CA:HyTiPVA pairs tuning their PBGs in different spectral regions of the fluorophore emission. Then, the DBRs were placed on the back side of the LSC with the aim to reflect photons leaving the slab from the escape cone (see Figure 1a). To obtain the best performances from the DBRs, their PBG should be spectrally tuned to the low energy side of the fluorophore emission and should have a large full width at half maximum (FWHM).^{25, 26} First, the spectral tuning and the angle of incidence dispersion of the PBG of the DBR allows the mirrors to work finely for all incidence geometry, i.e. for any daily sun illumination conditions.^{34, 35} Second, a PBG FWHM larger than the dye fluorescence spectrum is desirable to reflect all the light escaping from the slab. Both the PBG spectral tuning and width are mainly dictated by the periodicity and the dielectric contrast among the DBR components.³⁴ In a more detail, the PBG position is commonly controlled engineering the layer thicknesses, while its spectral width is only dictated by the dielectric contrast of the materials used. Large dielectric contrast inorganic DBR structures usually gather the best performances,²⁶ while commodity polymers provide reduced dielectric contrast, but allow very light and flexible mirrors, that can be fabricated even on square meter area (Figure 1c).^{34, 36-43} To increase the dielectric contrast in polymer structures, several issues mainly due to the constraint of mutual processability have to be tackled.^{28-30, 44, 45} Indeed, developing suitable high index systems is not straightforward,^{33, 45-49} while the use of low refractive index polymers suitable for solution growth of DBRs is very complex.^{33, 47} Only two strategies, which show relevant drawbacks, have been reported so far. For instance, highly porous polymers have very low refractive index,^{50, 51} but their

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high void volume fraction prevents their use for the fabrication of DBR due to percolation of the high index counterpart within the porosity. Low refractive index perfluorinated polymers have been instead successfully employed to spun-cast DBRs,^{33, 47} but the cost of such materials is very high and their processability requires specific know-how to allow fine spectral tuning and surface wettability. For these reasons, we decided to use CA as the low refractive index material for DBR fabrication, in fact it is widely employed and easily processable.³⁴ The refractive index of CA is about 1.47 over a broad spectral region (black line in Figure 3a). In this range, the polymer thin film does not show absorption bands assigned to electronic transitions, which makes it well suitable as transparent material for DBR fabrication. In DBR series P we coupled CA to PVK, which shows instead relevant absorption below 300 nm and a refractive index value of about 1.67 (green line in Figure 3a). Indeed, CA and PVK have been often coupled in literature for the fabrication of polymer DBR for different applications.³⁴ However, coupling CA and PVK does not allow to achieve dielectric contrast larger than 0.21, thus limiting the PBG bandwidth. Moreover, a very large number of periods is necessary to gather reflectance values close to unity.^{30, 34, 46}

One of the most promising strategies to achieve large refractive index in polymer matrices consists in the loading of high refractive index nanofillers such as Titania nanoparticles ($n=2.5$).⁵⁵ To strongly increase \tilde{n} in nanocomposites suitable for photonics two requirements are mandatory. First, large nanofiller volume fractions are needed. Second, a very small size of nanoparticles and no tendency to aggregation are necessary to prevent light scattering and maintain the device transparency. The combination of these requirements, joined to the need for high solution processability, makes this approach challenging.⁵⁶ We developed a new processable material with refractive index above the one of PVK, which is currently the solution-processable commodity polymer with the largest refractive index over a very broad spectral range.^{53, 54} To this end, we refined a method previously reported to strongly increase the refractive index of PVA grafting hydrated Titania directly to the hydroxylic group of the polymer.^{49, 52} PVA is indeed particularly appealing owing to the large amount of hydroxylic substituents - which can be used as grafting sites for the nanofiller, thus acting as spacers - drastically reducing the aggregation processes and eliminating the need for surfactants (see Methods Section).⁵⁷⁵⁸ We then use the new HyTiPVA and CA to spin-cast a series (H) of high performance DBRs with PBG easily tunable on the emission spectrum of the LSC fluorophore. The optical response of the new HyTiPVA material has been determined by spectroscopic ellipsometry and the real part (n) of the complex refractive index ($\tilde{n}=n+ik$) is shown in Figure 3a and compared with other polymers used in this work. The loading results in a dramatic increase of the PVA refractive index. Indeed, while bare PVA shows a refractive index of about 1.55 in the analyzed spectral range (red dashed line in Figure 3a), after the loading the HyTi, the index approaches 1.9 over the entire near infrared and visible spectral regions (red curve in Figure 3a). The full spectral response of \tilde{n} is shown in Supporting Information S2. From the spectrum reported in Figure 3a, according to a simple Maxwell-Garnett

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effective medium model⁵⁹ and considering the refractive index of the HyTi equal to the one of anatase TiO₂, we estimated volume fraction load of at least 30%. Moreover, no absorption due to electronic transition is detected in the sample spectral range (see also Supporting Information Figure S2). These characteristics, together with the good processability of PVA, make the new composite a promising high refractive index medium to be coupled with CA.

The high refractive index of the HyTiPVA hybrid has a remarkable effect on the PBG FWHM. Figures 3b and c compare the reflectance spectra of two DBRs made of CA and the high refractive index polymers (HyTiPVA, sample H1 in panel b; PVK, sample P1 in panel c). The reflectance spectra of the sample H1 measured in nine different spots of the sample surface show a large reflectance peak centered at 750 nm with a FWHM of 170 nm, followed by a second order peak centered at 377 nm (Figure 3b, more spectral information and photographs are shown in Supporting Information Figure S3). Due to the deposition process, the central spot of the sample surface (spot N. 5) commonly differs from the others, affecting the surface homogeneity.²⁷ On the other hand, the nice overlap of the other spectra, together with the interference pattern testifies the homogeneity and the good optical quality of the sample. The presence of the second order PBG indicates that the mirrors do not fulfill the lambda fourth condition often used for laser cavities,³⁴ thus possibly allowing wider FWHM. The background provides an average reflectance of about 10%. Comparing the reflectance spectra of the H1 DBR to the LSC emission and transmittance (Figure 2b, the emission spectrum is also highlighted in orange in Figure 3b and 3c), we notice the tuning of the first order PBG in the emission spectral region and to its low energy side. DBRs with PBG tuned in different regions have also been fabricated and tested as reported in Supporting Information Figure S4 for samples H2-H8.

The CA:PVK DBR is instead characterized by a first order PBG at 660 nm with FWHM of 70 nm, positioned on the low energy side of the fluorophore emission (Figure 3c). The second order PBG in this case has a very low intensity and is slightly visible only in two over nine spots measured, demonstrating that the sample is matching the lambda fourth condition.^{29, 34} More spectral info and images of this sample are reported in Supporting Information Figure S5. Comparing the spectra of Figure 3b and c we notice that the CA:PVK sample is less homogeneous than the one fabricated using the HyTiPVA nanocomposite. Moreover, the PBG intensity and width are smaller than for the CA:HyTi:PVA DBR but, as shown in the following, this sample provides the best performances when applied to the LSC. Supporting Information Figure S6 displays the optical characterization of the other samples of the series (P2-P8).

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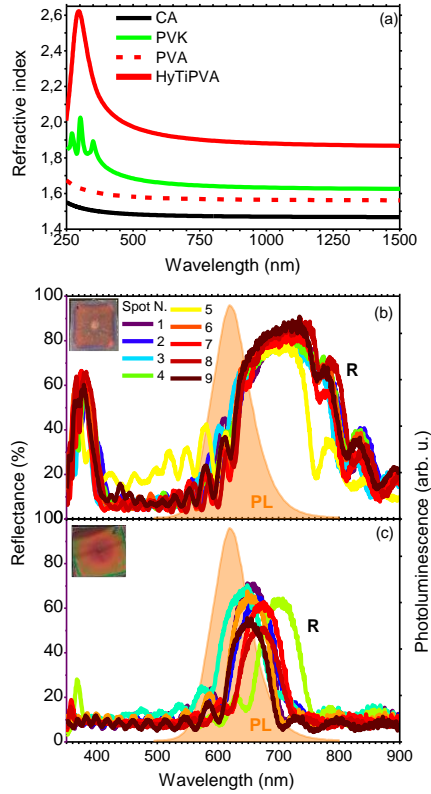


Figure 3. (a) Refractive index of CA (black line), PVK (green line) from literature,^{53, 54, 60} PVA (red dashed line) and HyTiPVA (red line) as retrieved from ellipsometry measurements. (b, c) Reflectance spectra over nine different positions of the polymer DBRs made by CA-HyTiPVA and CA-PVK, respectively.

For what concern the performances of the SilaFluo-LSCs, we will first focus on devices with size $24 \times 24 \times 3 \text{ mm}^3$. These LSCs have a geometrical factor, that is the ratio between the illuminated surface area and the solar cell area, $G=8$. As described before, a diffuser layer is mounted on the back of the reference LSC with an air gap to prevent propagation losses (constant η_{WG}). To assess the DBR effect on the LSC performances we used optical efficiency (η_{opt}^{LSC}) of the side cells integrated spectrally:^{61, 62}

$$\eta_{opt}^{LSC} = \frac{c}{G} \quad (3)$$

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where C is the concentration factor, that is the ratio between the maximum current of the PV cell attached the LSC edges under standard solar simulator illumination and the maximum current of the bare cell placed perpendicularly to the lamp.^{61, 62}

For the reference LSC, we found an optical efficiency of 9.4% (Figure 4) with $C=0.75$, in full agreement with our recent findings.¹⁵ We then replaced the diffusing layer with CA-HyTiPVA (samples H). The new systems show optical efficiencies ranging from 9.4% to 10.3% with mean 9.7% and standard deviation $\sigma=0.4\%$, that is up to a 10% enhancement factor. When the diffuser is replaced with the P series of DBRs (CA-PVK), the devices optical efficiency retrieved is more heterogenous and ranges from 9.3%, which is lower than the reference efficiency, to 10.6%, which represent the best enhancement achieved, the mean value achieved being 9.7% with $\sigma=0.5\%$.

The larger homogeneity of the data obtained for the H series, can be explained by considering the PBG reflectance intensity and FWHM of the two systems. For the H series, the larger dielectric contrast with respect to the samples prepared with PVK allows wider PBGs, and in turn their overlapping to the largest part of the fluorophore emission spectrum, even for different PBG tuning, making the H series very efficient reflectors for photons leaving the slab within the escape cone (Figure 1). Then, notwithstanding possible tuning errors and small PBG reflectance value of some of the samples (See for instance sample H7 in Supporting Information Figure S4) at the PBG, all the samples prepared with the HyTiPVA composite perform better than the reference sample with the diffuser. In particular, those samples tuned on the low energy side of fluorophore emission and with larger FWHM (H1, H6, H8) provide the best enhancements of optical efficiency due to photon recycling at light angle of incidence far from the normal direction. Conversely, for CA:PVK DBRs of the series P, both the PBG reflectance intensity and FWHM are relatively small. This characteristic makes the efficiency of the photon recycling more sensitive to the spectral tuning of the photonic structure. These results demonstrate that either a high dielectric contrast or a fine tuning of the photonic structure is necessary to achieve a significant enhancement of the LSC optical efficiency using spun-cast polymer DBRs. We would like to stress that polymer DBRs shows a substantial advantage over standard mirrors used for LSC. Indeed these structures are much lighter and are easily adaptable to any surface (even curved if requested, Figure 1c), and can be eventually grown by different techniques, coextrusion, over square meters at industrial level.^{34, 37-39, 63, 64}

To evaluate the scale-up opportunities of our approach, we also tested the DBRs in mosaic configuration on larger LSC, e.g. by doubling LSC lateral size ($G=16$). In this case, we created a DBR mosaic coupling the larger LSC to 4 DBR mirrors. Figure 4b shows that for the larger device when the diffuser is used the device optical efficiency does not differ from the previous case. We then exchanged the diffuser with the four-best performing DBRs for each of the two series thus enhancing the efficiency to 10.2% and 10.3% for the H and P series, respectively. Such enhancement, which

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corresponds to a $\sim 9.5\%$ increase is impressive considering the detrimental effects of the DBR edges, which are known to reduce the LSC performances.⁷ Again, the use of industrial techniques previously highlighted for large area DBR production could be of great help to scale-up the dimension of LSC, thus making them a widespread and successful technology.

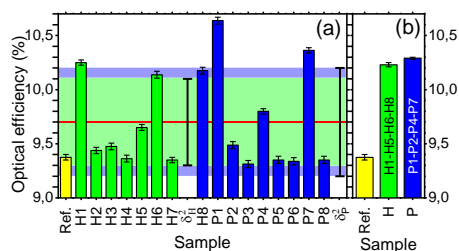


Figure 4. (a) LSC optical efficiency: reference LSC (yellow bars); LSC with applied DBR of the H (green bars) and P series (blue bars). (b) Optical efficiency for LSC with mosaic DBR mirror. The double arrow shows η for the two series of DBRs.

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Conclusions

We demonstrated that polymer DBRs made of commodity polymers including CA as low index medium and PVK or HyTi-PVA nanocomposite fabricated *ad-hoc* by simple wet chemistry can enhance LSCs optical efficiency up to a $\sim 10\%$ increase when used as back reflectors with respect to the same system with a standard diffuser. Moreover, we proved that the enhancement is retained scaling-up of the device area by a factor 4 and using the DBR back reflectors in mosaic configuration. The transparency in the largest part of the visible spectral range of the LSC-DBR devices, together with the possibility to fabricate these systems on the square meter area using industrial techniques pave the way to their application in integrated photovoltaic systems for zero energy consumption buildings in the near future.

Methods

Fluorophore synthesis and characterization: SilaFluo was synthesized according to literature.¹⁵ Absorption and reflectance spectra were measured at room temperature by an Agilent Cary5000 UV-Vis-NIR spectrophotometer equipped with an Internal Diffuse Reflectance DRA-2500. Fluorescence spectra were measured at room temperature by a Horiba Jobin-Yvon Fluorolog®-3 spectrofluorometer equipped with a 450 W Xenon arc lamp and single and double grating excitation and emission monochromators, respectively.

LSC preparation: To prepare the fluorophore-PMMA layer, about 30 mg of PMMA and SilaFluo were dissolved in ~ 0.8 mL of chloroform and stirred for 30 min at room temperature. Subsequently, the

solution was spread out evenly on thoroughly cleaned 35x50 mm glass surface to obtain a film with thickness 25 ± 5 μm (Starrett micrometer) after evaporation at room temperature in a closed environment. The polymer film was then removed after immersion in water and stored in a desiccator for successive measurements by attaching them on 24x24x3 mm (geometrical factor, $G = 8$) or 50x50x3 mm ($G = 16.7$) cleaned glass (Edmund Optics Ltd BOROFLOAT window) with a high-purity silicone oil (poly(methylphenyl siloxane), 710 fluid, Aldrich, $n = 1.5365$) layer. The diffuser and the DBRs or DBR mosaic (4 DBRs) were placed beneath the LSC with $G = 8$ ($G=16.7$).

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Preparation of HyTiPVA: the HyTi composite was prepared mixing aqueous solutions of PVA and HyTi with different concentrations adapting a wet synthetic protocol previously reported.⁴⁹ HyTi solutions were previously obtained through a controlled hydrolysis of commercial TiCl_4 (Sigma-Aldrich, purity >99%) by slow addition of 8 ml of iced TiCl_4 to 62.5 ml of water. The mixtures were maintained under constant stirring at room temperature for 12 h to ensure full reaction. A clear colorless HyTi solution with Ti concentration of 1.03 mmol/L were obtained. To produce the hybrid material, the freshly-prepared HyTi solutions were added to a 20 g/L aqueous solution of PVA (Sigma-Aldrich, ($\langle M_n \rangle = 1.66 \times 10^5$ g/mol, 99+% hydrolyzed) at a constant ratio of 1.4:1 v/v. The samples were transparent in the Vis-NIR spectral interval (Supporting Information Figure S1), and solution-processable for the preparation of spin-coated films. To this purpose, the filmability of hybrid solutions was optimized by addition of EtOH in the ratio of 1:2 v/v before the mixture deposition.

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Polymer DBRs: P series DBR were prepared by spin-coating CA (Aldrich, $M_n = 30\,000$) dissolved in diacetone alcohol (35mg/mL) and PVK (ACROS Organic, $M_n = 56\,400$ $M_w = 135\,600$) toluene solutions (28mg/mL) on poly (ethylene terephthalate) (PET) substrates, the rotation speed was kept between 80 and 105 RPS. H series DBR were prepared by casting alternated layers of HyTiPVA and the CA solution on glass substrates with rotation speed ranging between 80 and 120 RPS.

More details are reported in Supporting Information Table 1.

LSC optical efficiency: The optical efficiency of the LSC was measured with a home-built equipment setup. Each DBR, single or mosaic, was placed beneath the LSC of $G = 8$ or $G = 16$, respectively. Each sample was tested in triplicate. A solar simulating lamp (ORIEL® LCS-100 solar simulator 94011A S/N: 322, AM1.5G std filter: 69 mW/cm^2 at 254 mm) was housed 27.5 cm above the sample. The PV module (IXYS SLMD121H08L mono solar cell 86 x 14 mm) was connected to a digital potentiometer (AD5242) controlled via I2C by an Arduino Uno micro-controller using I2C master library.⁶⁵ A digital multimeter (KEITHLEY 2010) was connected in series with the circuit, between the photovoltaic module and the potentiometer, to collect the current as a function of the external load. Conversely, the voltage was measured by connecting the multimeter in parallel to the digital potentiometer.

Optical function characterization: Spectroscopic ellipsometry measurements have been performed on reference thin films of the different materials, by using a VASE instrument by J. A. Woollam Co. in the range (250 – 2500) nm at different angles of incidence from 60° to 75°. ⁶⁰ Transmittance at normal incidence has been also measured with a Varian Cary 6000i spectrometer in the spectral range (300 – 1800) nm. As a result, the complex refractive index $n+ik$ for all materials was evaluated by WVASE32® software, adopting oscillator models that guarantee for Kramers–Kronig consistency and effective-medium approximation for the HyTi:PVA nanocomposite.

ASSOCIATED CONTENT

Supporting Information. Additional information reported are: Hybrid Titania-PVA Nanocomposite Optical Constants (S1); Diffuser and LSC Characterization (S2); Optical characterization of the DBRs (S3); Optical Efficiency Measurement Details (S3).

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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Notes

Any additional relevant notes should be placed here.

ABBREVIATIONS

LSC, Luminescent Solar Concentrators; PhC, Photonic Crystals; PBG, Photonic Band Gap; NIR, Near Infrared; SilaFluo, red-emitting 2-amino-7-acceptor-9-silafluorene, where the amino group is $-N(CH_3)_2$ and the acceptor is $-CH_2C(CN)_2$; PET, poly(ethylene terephthalate); PMMA, poly(methyl

methacrylate); PVA, poly(vinyl alcohol); CA, Cellulose Acetate; PVK, poly(9-vinylcarbazole); G, Geometrical factor; C, concentration factor;

REFERENCES

1. V. Balzani; N. Armaroli, *Energy for a Sustainable World*. Wiley-VCH: Weinheim, 2010.
2. G. Galloro https://www.eniday.com/it/technology_it/eni-ray-plus-finestre-intelligenti/.
3. M. G. Debijs; P. P. C. Verbunt, Thirty Years of Luminescent Solar Concentrator Research: Solar Energy for the Built Environment, *Adv. Energy Mater.* 2012, 2, 12-35.
4. F. Meinardi, et al., Highly efficient large-area colourless luminescent solar concentrators using heavy-metal-free colloidal quantum dots, *Nature Nanotech.* 2015, 10, 878.
5. A. Bozzola, et al., A Multi-optical Collector of Sunlight Employing Luminescent Materials and Photonic Nanostructures, *Adv. Optical Mater.* 2016, 4, 147-155.
6. R. Fusco, et al., Hybrid concentrated photovoltaic device [Filing date: 27.01.2015.](#)
7. F. Meinardi, et al., Large-area luminescent solar concentrators based on 'Stokes-shift-engineered' nanocrystals in a mass-polymerized PMMA matrix, *Nature Photon.* 2014, 8, 392-399.
8. I. Coropceanu; M. G. Bawendi, Core/Shell Quantum Dot Based Luminescent Solar Concentrators with Reduced Reabsorption and Enhanced Efficiency, *Nano Lett.* 2014, 14, 4097-4101.
9. J. Mei, et al., Aggregation-Induced Emission: Together We Shine, United We Soar!, *Chem. Rev.* 2015, 115, 11718-11940.
10. A. Pucci, Luminescent Solar Concentrators Based on Aggregation Induced Emission, *Isr. J. Chem.* 2018, 58, 837-844.
11. R. Mori, et al., Luminescent solar concentrators based on PMMA films obtained from a red-emitting ATRP initiator, *Polym. Chem.* 2018, 9, 1168-1177.
12. D. Nisi, et al., Red-emitting AIEgen for luminescent solar concentrators, *Mater. Chem. Front* 2017, 1, 1406-1412.
13. F. Gianfaldoni, et al., A push-pull silafluorene fluorophore for highly efficient luminescent solar concentrators, *RSC Advances* 2017, 7, 37302-37309.
14. J. C. Goldschmidt, et al., Increasing the efficiency of fluorescent concentrator systems, *Sol. Energ. Mater. Sol. C.* 2009, 93, 176-182.
15. M. Carloti, et al., Enhancing Optical Efficiency of Thin-Film Luminescent Solar Concentrators by Combining Energy Transfer and Stacked Design, *J. Lumin.* 2016, 171, 215-220.
16. P. Minei, et al., Cost-effective solar concentrators based on red fluorescent Zn(ii)-salicylaldiminato complex, *RSC Advances* 2016, 6, 17474-17482.
17. F. Mateen, et al., Metal nanoparticles based stack structured plasmonic luminescent solar concentrator, *Sol. Energy* 2017, 155, 934-941.
18. J. C. Goldschmidt; S. Fischer, Upconversion for Photovoltaics – a Review of Materials, Devices and Concepts for Performance Enhancement, *Adv. Optical Mater.* 2015, 3, 510-535.
19. J. Gutmann, et al. In Emission of Rhodamine B in PMMA opals for luminescent solar concentrators, *SPIE Photonics Europe*, SPIE: 2012; p 7.
20. A.-L. Joudrier, et al., Modeling and Fabrication of Luminescent Solar Concentrators towards Photovoltaic Devices, *Energy Procedia* 2014, 60, 173-180.
21. C. Ryan, et al., Designing spectrally-selective mirrors for use in luminescent solar concentrators, *Journal of Optics* 2018, 20, 024009.
22. L. Xu, et al., Enhanced Photon Collection in Luminescent Solar Concentrators with Distributed Bragg Reflectors, *ACS Photonics* 2016, 3, 278-285.
23. P. Lova, et al., Polymer Distributed Bragg Reflectors for Vapor Sensing, *ACS Photonics* 2015, 2, 537-543.
24. P. Lova, et al., Label-free vapor selectivity in poly(p-phenylene oxide) photonic crystal sensors, *ACS Appl. Mater. Interfaces* 2016, 8, 31941-31950.
25. P. Lova, et al., All-Polymer Photonic Microcavities Doped with Perylene Bisimide J-Aggregates, *Adv. Optical Mater.* 2017, 5, 1700523.

Commented [UdMO21]: ?

26. G. Manfredi, et al., Directional Fluorescence Spectral Narrowing in All-Polymer Microcavities Doped with CdSe/CdS Dot-in-Rod Nanocrystals, *ACS Photonics* 2017, 4, 1761-1769.
27. P. Lova, et al., Engineering the Emission of Broadband 2D Perovskites by Polymer Distributed Bragg Reflectors, *ACS Photonics* 2018, 5, 867-874.
28. G. Manfredi, et al., Lasing from Dot-in-Rod Nanocrystals in Planar Polymer Microcavities *RSC Advances* 2018, 8, 13026.
29. P. Giusto, et al., Colorimetric Detection of Perfluorinated Compounds by All-Polymer Photonic Transducers, *ACS Omega* 2018, 3, 7517-7522.
30. P. Lova, et al., Advances in Functional Solution Processed Planar 1D Photonic Crystals, *Adv. Optical Mater.* 2018, in press, 0, 1800730.
31. *Organic and Hybrid Photonic Crystals*, Edited by D. Comoretto, ed. 1; Springer International Publishing (2015); pp XXI, pp 497.
32. S. Marie, et al., A widely tunable refractive index in a nanolayered photonic material, *Appl. Phys. Lett.* 2004, 84, 3621-3623.
33. T. Kazmierczak, et al., Polymeric One-Dimensional Photonic Crystals by Continuous Coextrusion, *Macromol. Rapid Commun.* 2007, 28, 2210-2216.
34. H. Song, et al., Continuous melt processing of all-polymer distributed feedback lasers, *J. Mater. Chem.* 2009, 19, 7520-7524.
35. Chameleonlab - <http://chameleonlab.nl/>. (accessed 31/01/2018).
36. TORAY - <http://www.toray.com/>. (accessed 31/01/2018).
37. <http://foliophotonics.com/> Retrieved on 30/05/2018.
38. 3M installation, <http://www.conveniencegroup.com/3m-dichroic-film-case-study>. (accessed 30/03/2018).
39. Chameleonlab Chameleonlab Building. <http://chameleonlab.nl/> (accessed 30/03/2018).
40. P. Lova; e. al., Determination of Vapor Diffusion Coefficient and Label-Free Selectivity by All-Polymer Distributed Bragg Reflectors, submitted 2018.
41. P. Lova, et al., Advances in Functional Solution Processed Planar Photonic Crystals, *Adv. Optical Mater.* 2018, in press DOI: 10.1002/adom.201800730R1.
42. S. Gazzo, et al., High refractive index hyperbranched polyvinylsulfides for planar one-dimensional all-polymer photonic crystals, *J. Polym. Sci. B: Polym. Phys.* 2016, 54, 73-80.
43. S. V. Radice, et al., One-dimensional planar photonic crystals including fluoropolymer compositions and corresponding fabrication methods, WO 2016/087439 A1, 2016.
44. T. S. Kleine, et al., One Dimensional Photonic Crystals Using Ultrahigh Refractive Index Chalcogenide Hybrid Inorganic/Organic Polymers, *ACS Macro Letters* 2018, 7, 875-880.
45. M. Russo, et al., One-pot synthesis of polymer/inorganic hybrids: toward readily accessible, low-loss, and highly tunable refractive index materials and patterns, *J. Polym. Sci. B: Polym. Phys.* 2012, 50, 65-74.
46. W. Gaëtan, et al., Nanoporous films with low refractive index for large surface broad-band anti-reflection coatings, *Macromol. Chem. Phys.* 2010, 295, 628-636.
47. J. Q. Xi, et al., Optical thin-film materials with low refractive index for broadband elimination of Fresnel reflection, *Nat. Photon.* 2007, 1, 176-179.
48. M. Russo, et al., Pronounced photochromism of titanium oxide hydrates (hydrous TiO₂), *J. Mater. Chem.* 2010, 20, 1348-1356.
49. L. Frezza, et al., Directional Enhancement of Spontaneous Emission in Polymer Flexible Microcavities, *J. Phys. Chem. C* 2011, 115, 19939-19946.
50. L. Fornasari, et al., Demonstration of fluorescence enhancement via Bloch surface waves in all-polymer multilayer structures, *Phys. Chem. Chem. Phys.* 2016, 18, 14086-14093.
51. WVASE32® software & database by J. A. Woollam Co. Inc.
52. J.-g. Liu; M. Ueda, High refractive index polymers: fundamental research and practical applications, *J. Mater. Chem.* 2009, 19, 8907-8919.
53. T. Yovcheva, et al., Refractive index investigation of poly(vinyl alcohol) films with TiO₂ nanoparticle inclusions, *Appl. Opt.* 2012, 51, 7771-7775.
54. S. Mahendia, et al., Tuning of refractive index of poly(vinyl alcohol): Effect of embedding Cu and Ag nanoparticles, *J. Appl. Phys.* 2013, 113, 073103.
55. G. Russell J.; B. Robert W., *Optical Properties of Nanostructured Optical Materials*, *Chem. Mater.* 1996, 8, 1807-1819.

Commented [UdMO22]: già Ref. 30?

Commented [UdMO23]:

56. Z. Krumer, et al., Compensation of self-absorption losses in luminescent solar concentrators by increasing luminophore concentration, *Sol. Energ. Mater. Sol. C.* 2017, 167, 133-139.
57. Y. Zhao; R. R. Lunt, Transparent Luminescent Solar Concentrators for Large-Area Solar Windows Enabled by Massive Stokes-Shift Nanocluster Phosphors, *Adv. Energy Mater.* 2013, 3, 1143-1148.
58. TORAY <http://www.toray.com> (accessed (accessed: January 2018)).
59. 3M 3M installation. <http://www.conveniencegroup.com/3m-dichroicfilm-case-study> (accessed (accessed: March 2018)).