This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal’s standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.
Efficient bifacial dye-sensitized solar cells through disorder by design

José M. Miranda-Muñoz, Sol Carretero-Palacios, Alberto Jiménez-Solano, Yuelong Li, Gabriel Lozano and Hernán Míguez*

Herein we realize an optical design that optimizes the performance of bifacial solar cells without modifying any of the usually employed components. In order to do so, dielectric scatterers of controlled size and shape have been successfully integrated in the working electrodes of dye-sensitized solar cells (DSSCs), resulting in bifacial devices of outstanding performance. Power conversion efficiencies (PCE) as high as 6.7% and 5.4% have been attained under front and rear illumination, respectively, which represent a 25% and a 33% PCE enhancement with respect to an 8 µm-thick standard solar cell electrode using platinum as catalytic material. The remarkable bifacial character of our approach is demonstrated by the high rear/front efficiency ratio attained, around 80%, which is among the largest reported for this sort of devices. The proposed optimized design is based on a Monte Carlo approach in which the multiple scattering of the light within the cell is fully accounted for. We identify the spherical shape of the scatterers as the key parameter controlling the angular distribution of the scattering, being the most efficient devices those in which the inclusions provide a narrow forward-oriented angular distribution of the scattered light.

Introduction

Serious efforts have been devoted towards the enhancement of dye-sensitized solar cell (DSSC) performance, whose fabrication processes and operation possibilities make them an attractive alternative for specific applications where cost-effective, solution-processed, transparent or aesthetically attractive solar cells are sought after. In contrast to other emerging photovoltaic devices, dye-sensitized technology features considerable stability.4-6 Solar modules have been built with them7,8 and successfully integrated as architectural elements. Bifacial solar cells, i.e., photovoltaic devices conceived for operation under both front and rear illumination, simultaneously or sequentially, have been proposed as an effective means towards cost reduction, as a same-area cell is able to harvest a higher fraction of light,9 concomitantly facing the drawbacks derived from the sun motion during daytime, an issue frequently regarded when aiming at outdoor applications. Since the first demonstration of a bifacial DSSC,10 different routes aiming to improving charge transport and light harvesting efficiency have been reported.11,12 Most of the efforts have been devoted to increasing the amount of light that reaches the photoanode when the cell is illuminated from the rear side, by employing more transparent hole-collecting systems.11-22 From a different perspective, optical structures, integrated either inside 23-25 or outside26-31 the sensitized film, have proven to be very effective at enhancing light harvesting efficiency for operation under front illumination at those wavelengths where the absorption cross section of the dye decreases. In particular, high performance DSSCs have been reported for devices integrating either a porous back-scattering film 32,36 or submicron particles of high refractive index in the mesoporous TiO2 matrix, profiting from the multiple scattering to increase the optical path of the incident light and therefore the probability of light to be absorbed.33,36-41 Earlier experimental proposals based on this idea have considered polyhedral and irregular scattering centres, which lead to light scattered within a broad angular range when averaged over the possible random orientations of the centres. Consequently, optical losses occur at regions close to the entrance of the solar cell.42,43 Such photonic architectures have targeted the standard one-side illumination DSSCs, but no optical design to optimize the absorption of light under bifacial illumination conditions has been proposed so far.

Herein, spherical submicron TiO2 particles are randomly dispersed in the sensitized film of a DSSC in a bifacial configuration as a means for boosting absorbance. TiO2 scatterers are considered because they present enough refractive index contrast, so as to lead to efficient light scattering when embedded in the system comprised of the mesoporous TiO2 matrix immersed in the electrolyte. Specifically, the scattering efficiency and the angular distribution of the light scattered by the individual nanoparticles can be accurately controlled through their dimension and shape. The integration of TiO2 scattering centres is performed according to a design obtained from an accurate theoretical model that serves as a precise guide for
the experiments. We demonstrate that a careful choice of the size of the TiO$_2$ inclusions within the sensitized film together with a proper particle number density (ff, that is, the ratio of the total volume occupied by the scattering centres to the total volume of the active layer), enable optimized DSSCs. In this way, light harvesting, and hence the performance of devices, is enhanced irrespective on the illumination side. We achieve PCE values as high as 6.7% for front illumination and 5.4% for rear illumination incorporating 200-nm radius spherical TiO$_2$ nanoparticles in 8 µm-thick electrodes using ff = 10%. This represents a 25% and a 33% efficiency enhancement for front and rear illumination, respectively, in comparison to a standard cell of same thickness. Such front value is comparable to the efficiency of a device of similar thickness integrating a standard back scattering layer. The route for absorption improvement presented here exclusively involves modifications in the active layer of the device, i.e., the sensitized mesostructured nanocrystalline TiO$_2$ film. Our proposal is therefore fully compatible with alternative approaches already proposed in the literature$^{11-22}$ for superior performance of the cell under rear illumination, which paves the way for the demonstration of bifacial cells with record efficiency.

Methods

Theoretical modelling

Angular scattering distribution and scattering efficiency simulations: absorption and scattering of light by spherical particles was semi-analytically evaluated through scattering Mie theory.$^{46,47}$ For other shapes, 3-dimensional Finite-Difference Time-Domain (FDTD) simulations employing the software “FDTD Solutions” from Lumerical Solutions were performed to calculate the angular scattering distribution and scattering efficiency. A hollow with the same shape as the particle between the scattering centre and the embedding medium can be included in both semi-analytical and numerical calculations to account for shrinkage effects observed experimentally. Core-shell particles are considered, so that a TiO$_2$ nanoparticle surrounded by an electrolyte-filled shell acts as a scattering centre embedded in an external absorbing medium, comprised of mesoporous sensitized TiO$_2$ infiltrated with electrolyte. The spectral complex refractive index of the materials employed to model the scattering system (TiO$_2$ nanoparticle and electrolyte shell), and the external absorbing medium, in both semi-analytical and numerical calculations, are available in the Supplementary Information, Fig. S1.

To numerically calculate the absorption and scattering efficiencies and the angular distribution of light scattering of individual particles, FDTD simulations employing a simulation box size of 1.0×1.0×1.0 µm$^3$ with perfectly matched layer conditions on every boundary were performed. The volume of all particles considered in the numerical simulations is the same as that of a spherical particle of radius $r = 150$ nm, with slight volume variations in the case of irregular shapes. A plane wave of incident wavelength $\lambda = 650$ nm was considered. In the case of irregular shapes (truncated pyramids and distorted cubes), several angles and sides of illumination were examined. The mesh grid was set to be 150 nm over the entire simulation volume, with a refinement of 4 nm over a $0.72\times0.72\times0.72$ µm$^3$ volume spanned, over and around, the volume occupied by the core-shell nanoparticle, providing converged results for all particle shapes considered. The total-field scattered-field method was used to directly calculate the scattered power by means of frequency-domain transmission monitors positioned in the scattered field region.

Light harvesting efficiency calculation: For these calculations we employ a Monte Carlo approach in which the trajectory of individual photons impinging the cell is fully accounted for.$^{17,38,48,49}$ The cell is represented as a 3-dimensional multilayer structure, each layer characterized by the corresponding thickness and spectral complex refractive indexes of all materials comprising it. In addition, if a layer includes several materials, as in the case of the mesoporous TiO$_2$ layer, additional input parameters are required: ff, and particle size of light scatterers. The trajectory of 10$^7$ photons per wavelength, a number yielding converged results, is determined by Fresnel coefficients at the interface of two layers, and by Mie theory if light scatterers are included. In contrast to previous approaches,$^{17,38,48,49}$ here we include the external absorbing medium when evaluating the diffuse dispersion and absorption of light described by Mie theory. By collecting all photons finishing their trajectory at the incoming and outgoing media, information of reflectance and transmittance is retrieved, distinguishing diffuse light through the photon exit angle. In the same way, the photons collected by the different absorbing materials in the cell provide information of productive (light absorbed by dye molecules) and parasitic (light absorbed by any other material in the cell) absorbance. Moreover, spatial knowledge of absorption events by dye molecules allows us to calculate the so-called electron generation function, or spectral light absorption, and electron generation function (IPCE) according to the incident photon to current efficiency, and IPCE, and electron generation function (IPCE) are computed without employing any fitting parameter.

Short-circuit current density calculation: For the generation of maximum short-circuit current density ($J_{sc}$), we assumed $\eta_{IPCE} = \eta_{IPCE}^0$, where $\eta_{IPCE}^0$ corresponds to the incident photon to current efficiency, and $\eta_{IPCE}$ is the spectral light harvesting efficiency. Consequently, the value of $J_{sc}$ is exclusively dependent on the productive absorption in the electrode, which implies that the collection and the injection efficiencies are considered to be 100%. In this way, such calculations render an upper limit for the values of $J_{sc}$, the ideal situation when each photon absorbed by the dye contributes to the photocurrent.

Preparation of TiO$_2$ pastes with TiO$_2$ scattering centres

The nanospheres used as scattering centres, synthesized according to a well established reported procedure,$^{50}$ were dispersed in a small volume of ethanol absolute. After determination of its concentration and that for the commercial paste we used for the generation of the mesoporous TiO$_2$ matrix of the electrode (18-NRT, Dyesol, made of irregular particles of average size of ca. 20 nm), we proceeded to prepare pastes with total 0.5 g TiO$_2$ weight. The calculated amount for the commercial paste was first roughly dissolved in 5 ml ethanol absolute and, after brief sonication, the solution
was vigorously dispersed using a vortex mixer. Subsequent magnetic stirring process was carried out for 10 minutes. The calculated amount of the TiO$_2$ nanosphere solution was dropped in the mixture and 0.8257 g of α-terpineol (SAFC, ≥96%) that was used as the main solvent of the paste, were added, performing in-between addition the same mixing and stirring steps. Finally, the ethanol in the solution was evaporated at 70°C and around 80 mbar pressure using a Rotavapor set up (Büchi, R-200).

**Cell fabrication**

FTO glass substrates (XOP Glass, FTO TEC-11X) for the preparation of the photoanodes comprised of a 3-mm thick glass coated with a 575-nm thick FTO layer were cleaned by sonication in a 2% vol. Hellmanex solution in deionized water first and then in ethanol absolute. After that, the electrodes were coated on these substrates from the previously prepared pastes via screen-printing and 0.25 cm$^2$ homogenous 8-µm thick layers resulted after several depositions. For the preparation of the scattering layer we used a commercial paste containing large TiO$_2$ particles (WER2-O, Dyesol, made of irregular particles of average size comprised between ca. 150 nm and ca. 250 nm) for deposition on top of the corresponding sintered electrode. The photoanodes were sintered and immersed overnight in a 0.5 mM solution of dye (N719, Dyesol) in ethanol absolute in order to sensitise the films. For the preparation of the counterelectrodes, clean FTO glass substrates drilled for the subsequent electrolyte injection were spin-coated using a 0.6mM chloroplatinic acid hexahydrate (Sigma Aldrich, ≥37.50%) solution in 2-propanol. The process of coating was previously optimized for maximum homogenous 8-µm particles (WER2-O, Dyesol, made of irregular particles of average size comprised between ca. 150 nm and ca. 250 nm) for deposition on top of the corresponding sintered electrode. The photoanodes were sintered and immersed overnight in a 0.5 mM solution of dye (N719, Dyesol) in ethanol absolute in order to sensitise the films. For the preparation of the counter-electrodes, clean FTO glass substrates drilled for the subsequent electrolyte injection were spin-coated using a 0.6mM chloroplatinic acid hexahydrate (Sigma Aldrich, ≥37.50%) solution in 2-propanol. The process of coating was previously optimized for maximum homogenous 8-µm thick layers resulted after several depositions. For the preparation of the scattering layer we used a commercial paste containing large TiO$_2$ particles (WER2-O, Dyesol, made of irregular particles of average size comprised between ca. 150 nm and ca. 250 nm) for deposition on top of the corresponding sintered electrode. The photoanodes were sintered and immersed overnight in a 0.5 mM solution of dye (N719, Dyesol) in ethanol absolute in order to sensitise the films. For the preparation of the counter-electrodes, clean FTO glass substrates drilled for the subsequent electrolyte injection were spin-coated using a 0.6mM chloroplatinic acid hexahydrate (Sigma Aldrich, ≥37.50%) solution in 2-propanol. The process of coating was previously optimized for maximum homogenous 8-µm thick layers resulted after several depositions. For the preparation of the scattering layer we used a commercial paste containing large TiO$_2$ particles (WER2-O, Dyesol, made of irregular particles of average size comprised between ca. 150 nm and ca. 250 nm) for deposition on top of the corresponding sintered electrode. The photoanodes were sintered and immersed overnight in a 0.5 mM solution of dye (N719, Dyesol) in ethanol absolute in order to sensitise the films.

For the preparation of the counter-electrodes, clean FTO glass substrates drilled for the subsequent electrolyte injection were spin-coated using a 0.6mM chloroplatinic acid hexahydrate (Sigma Aldrich, ≥37.50%) solution in 2-propanol. The process of coating was previously optimized for maximum homogenous 8-µm thick layers resulted after several depositions. For the preparation of the scattering layer we used a commercial paste containing large TiO$_2$ particles (WER2-O, Dyesol, made of irregular particles of average size comprised between ca. 150 nm and ca. 250 nm) for deposition on top of the corresponding sintered electrode. The photoanodes were sintered and immersed overnight in a 0.5 mM solution of dye (N719, Dyesol) in ethanol absolute in order to sensitise the films. For the preparation of the counter-electrodes, clean FTO glass substrates drilled for the subsequent electrolyte injection were spin-coated using a 0.6mM chloroplatinic acid hexahydrate (Sigma Aldrich, ≥37.50%) solution in 2-propanol. The process of coating was previously optimized for maximum homogenous 8-µm thick layers resulted after several depositions. For the preparation of the scattering layer we used a commercial paste containing large TiO$_2$ particles (WER2-O, Dyesol, made of irregular particles of average size comprised between ca. 150 nm and ca. 250 nm) for deposition on top of the corresponding sintered electrode. The photoanodes were sintered and immersed overnight in a 0.5 mM solution of dye (N719, Dyesol) in ethanol absolute in order to sensitise the films.

**Cell fabrication**

FTO glass substrates (XOP Glass, FTO TEC-11X) for the preparation of the photoanodes comprised of a 3-mm thick glass coated with a 575-nm thick FTO layer were cleaned by sonication in a 2% vol. Hellmanex solution in deionized water first and then in ethanol absolute. After that, the electrodes were coated on these substrates from the previously prepared pastes via screen-printing and 0.25 cm$^2$ homogenous 8-µm thick layers resulted after several depositions. For the preparation of the scattering layer we used a commercial paste containing large TiO$_2$ particles (WER2-O, Dyesol, made of irregular particles of average size comprised between ca. 150 nm and ca. 250 nm) for deposition on top of the corresponding sintered electrode. The photoanodes were sintered and immersed overnight in a 0.5 mM solution of dye (N719, Dyesol) in ethanol absolute in order to sensitise the films.

**Cell fabrication**

FTO glass substrates (XOP Glass, FTO TEC-11X) for the preparation of the photoanodes comprised of a 3-mm thick glass coated with a 575-nm thick FTO layer were cleaned by sonication in a 2% vol. Hellmanex solution in deionized water first and then in ethanol absolute. After that, the electrodes were coated on these substrates from the previously prepared pastes via screen-printing and 0.25 cm$^2$ homogenous 8-µm thick layers resulted after several depositions. For the preparation of the scattering layer we used a commercial paste containing large TiO$_2$ particles (WER2-O, Dyesol, made of irregular particles of average size comprised between ca. 150 nm and ca. 250 nm) for deposition on top of the corresponding sintered electrode. The photoanodes were sintered and immersed overnight in a 0.5 mM solution of dye (N719, Dyesol) in ethanol absolute in order to sensitise the films.

**Cell fabrication**

FTO glass substrates (XOP Glass, FTO TEC-11X) for the preparation of the photoanodes comprised of a 3-mm thick glass coated with a 575-nm thick FTO layer were cleaned by sonication in a 2% vol. Hellmanex solution in deionized water first and then in ethanol absolute. After that, the electrodes were coated on these substrates from the previously prepared pastes via screen-printing and 0.25 cm$^2$ homogenous 8-µm thick layers resulted after several depositions. For the preparation of the scattering layer we used a commercial paste containing large TiO$_2$ particles (WER2-O, Dyesol, made of irregular particles of average size comprised between ca. 150 nm and ca. 250 nm) for deposition on top of the corresponding sintered electrode. The photoanodes were sintered and immersed overnight in a 0.5 mM solution of dye (N719, Dyesol) in ethanol absolute in order to sensitise the films.

**Results and discussion**

We reported in a previous theoretical work the beneficial effects induced in a DSSC regarding light harvesting efficiency if randomly dispersed spherical inclusions are considered in the cell electrode. In light of these results, we focus herein on the influence of the implementation of this approach in DSSCs offering operation under front and rear side illumination using TiO$_2$ scattering centres. The shape of the inclusions critically affects the scattering of the light occurring inside the electrode. Figure 1(a) shows the angular distribution of light scattered by TiO$_2$ nanoparticles of diverse shapes (spheres, cubes, truncated pyramids and distorted cubes surrounded by an electrolyte-filled shell, as indicated in the inset schematics). The narrowest forward-oriented angular distributions are yielded when considering either a sphere or a cube, for which these turn to be almost identical. Moreover, spherical and cubical scatterers feature similar scattering efficiencies (see Fig. S3 in the Supplementary Information). Consequently, spherical and cubical scatterers direct light into deeper regions in the electrode very effectively while reflection losses owing to backward scattering at the entrance of the cell are significantly reduced. Notice that irregular shapes, e.g., a truncated pyramid or a distorted cube, yield a broader averaged angular distribution of the scattered light, even with considerable light scattering in backward directions. Despite the similar behaviour of the scattered light observed for a sphere and a cube, we focus on the former throughout the whole work, since spheres are experimentally easier to fabricate.

As displayed in Fig. 1(b), the system herein investigated consists of a mesoporous TiO$_2$ matrix incorporating spherical scattering centres and immersed in electrolyte, sandwiched between front and rear glass/FTO contacts, being the latter coated with a thin catalytic platinum layer. A zoom-in schematic of a cross section of the electrode is visible in Fig. 1(c), in which individual core-shell spheres are surrounded by the mesoporous TiO$_2$ matrix. We presume that this shell originates as a consequence of the shrinking of the nanocrystalline TiO$_2$ spheres during the sintering process of...
the film, as it can be seen in the Scanning Electron Microscopy (SEM) images displayed in Fig. 2. The optical effect of this shell is discussed in Fig. S4 of the Supplementary Information.

A plot of the scattering efficiencies for TiO$_2$ spheres with four different radii: 80 nm, 100 nm, 135 nm and 200 nm is presented in Fig. 1(d). In this range, the bigger the spheres are, the more efficient they become at scattering light. We have calculated (see Methods) the expected $J_{sc}$ values for a system comprising an 8-µm thick electrode containing spherical nanocrystalline TiO$_2$ inclusions of different size and in different concentrations under front, Fig. 1(e), and rear, Fig. 1(f), illumination. Data for scatterer sizes up to $r = 300$ nm and with filling fractions up to 20% are shown. The optimum configuration can already be met between these two upper limits for $r = 180$ nm and $ff_v = 19\%$, being $J_{sc} = 15.62$ mA·cm$^{-2}$ and $J_{sc} = 10.90$ mA·cm$^{-2}$ the maximum values attainable for front and rear illumination, respectively. So, according to these calculations, an enhancement around 35% in the upper limit value of $J_{sc}$ can be expected under operation by front illumination, and around 40% for rear, when comparing to a bare cell with no scattering centres ($ff_v = 0\%$). Note that the addition of the $J_{sc}$ values yielded by a device integrating a back scattering layer, $J_{sc} = 14.20$ mA·cm$^{-2}$ for front illumination, included as a dashed line in Fig. 1(e), and $J_{sc} = 3.87$ mA·cm$^{-2}$ for the rear, is close to that for a reference cell, which yields 11.69 mA·cm$^{-2}$ (front) and 7.83 mA·cm$^{-2}$ (rear). The comparison with a hypothetical system in which the angular distribution of the scattered light is assumed to be isotropic, while the scattering

Figure 1. (a) FDTD calculated angular distribution of light scattered by TiO$_2$ nanoparticles of the same volume embedded in a porous TiO$_2$ matrix at wavelength $\lambda = 650$ nm and averaged for different orientations of the scatterers with respect to the incident light. The dotted line corresponds to a sphere of radius $r = 150$ nm (i), the dashed line to a cube of side $L = 242$ nm (ii), the dash-dotted line refers to a truncated pyramid of hexagonal base (iii) and the solid line corresponds to a modified cube (iv). A shell with the same geometry as the nanoparticle filled with electrolyte is considered in all cases, with the same volume as that of a spherical shell of thickness $sh = 0.5r$ correspondingly. (b) Schematic of the solar cell architecture including scattering centres in the mesoporous TiO$_2$ matrix employed in the work. (c) Zoom-in of a cross section of the active layer of the device, showing the submicron TiO$_2$ particle system, comprised of a scattering sphere of radius $r$ and a shell of thickness $sh$, embedded in the mesoporous titania matrix. (d) Mie scattering efficiency spectra for spherical TiO$_2$ scattering centres with different sizes: $r = 80$ nm (solid black line), 100 nm (dotted grey line), 135 nm (dashed grey line), 200 nm (dot-dashed grey line) and $sh = 0.5r$ filled with electrolyte, all embedded in a porous TiO$_2$ matrix. (e), (f) Upper limit for the short-circuit current density of a simulated device under front and rear illumination, respectively, in relation to the filling fraction percentage and the radius value of the scattering centres. The black dashed line in panel (e) indicates the points of $J_{sc} = 14.20$ mA·cm$^{-2}$ corresponding to a device including a back-scattering layer. This same line has not been included in panel (f) due to its low value, 3.87 mA·cm$^{-2}$, which is evidently below that for the reference cell.
Electrodes containing different filling fractions of spherical scatterers of different size were prepared. In Fig. 2, three SEM images show the cross section of two 8-µm thick electrodes containing TiO$_2$ nanospheres with two different radii, namely, 100 nm and 200 nm and $f_f = 10\%$ for both. We notice the presence of a shell around the scatterers in all cases. Figure 2(c) provides a closer look at the film structure. SEM images of electrodes with varying filling fractions and sphere sizes are included in the Supplementary Information (see Fig. S6). In order to check the influence of both parameters, two sets of samples were prepared: one set with fixed value of the scatterer radius to 100 ± 15 nm and variable filling fraction from 5% to 15% and another set with 10% filling fraction and scatterer radius ranging from 100 to 200 nm. Figure 3(a) and 3(c) present the absorbance curves obtained for this system when illuminated from the rear side, that is, light impinging directly on the electrode. The films were screen printed on FTO/glass substrates. In all cases, we observe a broadband enhancement of the absorbance in the wavelength range comprised between ca. 600 nm and ca. 750 nm. Such increase results to be larger as the value of the given parameter, either filling fraction or scattering centre radius, becomes higher. The absorbance spectrum of a system with an electrode devoid of scattering centres has been included as a reference. Absorbance curves under front and rear illumination for a similar sample including a back scattering layer is shown as well for the sake of comparison. The corresponding theoretical curves are presented in panels 3(b) and 3(d), in which the sphere radius is taken to be $r = 80$ nm. The spherical nature of our dielectric scatterers, along with the fact that the nanoparticles are randomly distributed within the active layer, leads to an absorption enhancement that is independent on the illumination side (see Fig. S7 of the Supplementary Information).

We built solar cells for which maximum $J_{sc}$ is forecast following the predictions in panels 1(e) and 1(f) in Fig. 1. Measurements of the $\eta_{IPCE}$ as a function of $f_f$ were performed for both front and rear illumination, and are displayed in Fig. 4(a) and 4(b), respectively. A broadband enhancement when comparing to the reference cells is observed. This improvement in the $\eta_{IPCE}$ is visible mainly in the spectral range comprised between ca. 600 nm and 750 nm, as expected from the absorbance measurements presented in Fig. 3. It is important to notice how the trends observed under either front or rear illumination are qualitatively identical. The $J$-$V$ characteristics of the devices obtained for front and rear illumination when varying $f_f$ are also shown in Fig. 4(c) and 4(d), respectively. The curve corresponding to a cell including a back scattering layer is also presented for the sake of comparison. The inclusion of scattering centres leads to a significant enhancement in the value of $J_{sc}$ thus improving the performance of the device. Although these results exemplify well the effect of the approach herein proposed on the performance under both front and rear illumination, more details on the relation between film structure, optical properties and photovoltaic parameters can be found in the Supplementary Information (see Figs. S8 to S9).

The results obtained for several sets of cells varying the two given parameters, shown in Table 1, were averaged and only a representative curve of each type was shown for clarity. The observed trend is in accordance with that expected from the absorbance and $\eta_{IPCE}$ curves. PCEs are always above the...
ca. 5.4% attained for the bare reference cells under front illumination. Such enhancement is, in turn, larger as the filling fraction or the sphere radius increases. Maximum 6.7% efficiency associated to an averaged $J_{sc} = 13.54$ mA·cm$^{-2}$ is measured for the device including 200-nm radius nanocrystalline TiO$_2$ spheres with ff$_v = 10\%$ for front illumination, which corresponds to a theoretically estimated scattering mean free path $l_{sc} = 1.2$ µm at $\lambda = 650$ nm. Such short value, in comparison to the electrode thickness (8 µm), is consistent with the experimental observation of an enhancement of the absorptance. This means that several scattering events will occur before the light reaches the opposite side of the sensitized film. As a consequence, the path length of the light is increased and thus the probability for the incident radiation to be absorbed. The aforementioned efficiency improvement corresponds to a 25% enhancement with respect to the reference cell. Furthermore, this performance is above that observed from the measurements performed on cells including a back scattering layer under front illumination, with an averaged $J_{sc} = 12.70$ mA·cm$^{-2}$ and an efficiency of 6.3%, showing the potential for competitiveness of the approach herein proposed when compared to other standard methods for light harvesting enhancement that are valid only for one-side illumination. Lower $J_{sc}$ values are measured under rear-side operation, as expected, due to the smaller fraction of the incident light reaching the active layer owing to the additional layers absorbing and reflecting light, e.g., the thin catalytic platinum layer and the electrolyte layer, presenting the latter a significant absorptance peak near $\lambda = 400$ nm. Specifically, under rear illumination, a maximum $J_{sc} = 10.40$ mA·cm$^{-2}$ is measured for the device including 200-nm radius spherical scatterers with ff$_v = 10\%$, corresponding to a 5.4% PCE, which represents a 33% enhancement with respect to a bare cell. The measured $J_{sc}$ values increases with both the filling fraction and the scatterer size, displaying the same trend observed under front illumination. In contrast, the performance of devices including a back scattering layer strongly decreases for rear illumination, showing a limited 2.1% efficiency. Interestingly, if the use of thicker (~15 µm) sensitized films as those typically employed to achieve high efficiency bifacial cells is regarded as an option, our model predicts a rear and front side enhancement above 20%.

Figure 3. Absorptance curves of the system glass/FTO/8-µm electrode under rear illumination. (a) Experimental curves for different filling fraction values and 100 ± 15 nm scatterer radius. (b) Theoretical curves for different filling fraction values and 100 scatterer radius. Solid black line: reference, short-dotted grey line: ff$_v = 5\%$, short-dashed grey line: ff$_v = 7.5\%$, dash-dotted grey line: ff$_v = 10\%$, dashed grey line: ff$_v = 20\%$. Experimental curves for different sphere radii and 10% filling fraction. (d) Theoretical curves for different sphere radii and 10% filling fraction. Solid black line: reference, short-dotted grey line: 100 ± 15 nm radius, dash-dotted grey line: 135 ± 15 nm radius, dashed grey line: 200 ± 25 nm radius. Data regarding the absorptance in a system with no inclusions and a back scattering layer are included in (a) and (c), being the black dotted line the absorptance of the system under front illumination and the grey dotted line the absorptance under rear illumination.

Figure 4. Experimental incident photon to current efficiency ($\eta_{IPCE}$) and Current density-Voltage ($J-V$) curves for complete cells with different filling fraction values and 160 ± 50 nm scatterer radius. (a) $\eta_{IPCE}$ curves for front illumination. (b) $\eta_{IPCE}$ curves for rear illumination. (c) J-V characteristics for front illumination. (d) J-V characteristics for rear illumination. Solid black line: reference, short-dotted grey line: ff$_v = 5\%$, dash-dotted grey line: ff$_v = 10\%$, dashed grey line: ff$_v = 15\%$, dotted black line: cell with a back scattering layer. Electrode thickness: 8 µm.
Experimental observations indicate that there exists a maximum value of the volume occupied by the inclusions before the film suffers from mechanical instability or delamination. Consequently, it was not possible to fabricate electrodes containing big particles in a large loading fraction. However, the values attained within the limits imposed by fabrication are close to those found as optimal.

The values of the open circuit voltage ($V_{oc}$) and fill factor ($FF$) of the cells scarcely fluctuate, around $V_{oc}=760$ mV and $FF=65\%$ under front illumination, and $V_{oc}=750$ mV and $FF=68\%$ under rear illumination. Notice that such electrical parameters are in line with those for the state-of-the-art cells employing Pt as the catalytic material.\textsuperscript{10,13-17,19} Specially the $J_{sc}$ and PCE values attained for rear illumination are above most of those reported for this standard configuration of the cell, in spite of the fact that the active layers herein employed are approximately 50\% thinner than the ones for which the largest efficiencies attained are reported.\textsuperscript{10,12,13,15-17,19,21} Hence, a direct consequence of optimising the optical design of the bifacial cell is that we can reduce significantly the electrode thickness.

The independence of the enhancement achieved on the illumination side becomes even more visible when peering at the rear/front efficiency ratios in the last column of Table 1, which barely vary. This points out that the front and rear efficiencies increase with the particle size and loading in a similar way regardless the illumination conditions, indicating that the fabricated devices operate as improved bifacial cells. Such values prove our design is an effective route toward efficient bifacial performance, being amongst the largest values reported in the literature up to date for cells employing Pt as the material for the coating of the counter-electrode, and standard (<10 µm) film thickness.\textsuperscript{11-20} Moreover, most of the approaches reported in the literature to improve the efficiency of bifacial cells are compatible with the electrode modification we propose herein.

The experimental values attained for the $J_{sc}$ were contrasted with the upper limit predicted by the model, from which a collection efficiency value near 90\% could be estimated, consistent with the 18-µm electron diffusion length theoretically assessed from the fitting of the experimental $\eta_{PCE}$ curves (please see Figs. S10 and S11 in the Supplementary Information). Most importantly, the inclusion of the nanocrystalline scatterers does not entail a significant decrease of the collection efficiency, which means they do not affect charge transport as it has been demonstrated in other

| Sample | illumination | $J_{sc\ exp.}$ | $V_{oc}$ | $FF$ | PCE | $\eta_{rear}/\eta_{front}$ |
|--------|--------------|----------------|---------|------|-----|--------------------------|
|        | Front        | 10.30 ±0.06    | 780±2   | 65.6±0.8 | 5.3±0.0 | 0.72±0.00               |
|        | Rear         | 7.19±0.02      | 773±4   | 69.3±0.2 | 3.8±0.0 | 0.74±0.11               |
| $ff_v = 5\%$ | Front       | 11.50±0.30     | 764±4   | 63.8±0.8 | 5.6±0.1 | 0.74±0.11               |
|        | Rear         | 8.20±0.30      | 752±1   | 67.1±0.3 | 4.2±0.2 | 0.74±0.09               |
| $ff_v = 10\%$ | Front       | 12.40±0.30     | 784±6   | 64.4±0.4 | 6.2±0.1 | 0.74±0.09               |
|        | Rear         | 8.68±0.16      | 779±5   | 68.1±0.6 | 4.6±0.1 | 0.74±0.08               |
| $ff_v = 15\%$ | Front       | 12.90±0.30     | 782±5   | 65.3±1.1 | 6.6±0.1 | 0.74±0.08               |
|        | Rear         | 9.30±0.40      | 768±4   | 68.1±0.8 | 4.9±0.2 | 0.74±0.08               |
| Back Scattering layer | Front | 12.70±0.40  | 762±8 | 64.6±0.4 | 6.3±0.1 | 0.34±0.03               |
|        | Rear         | 4.02±0.06      | 737±8   | 71.8±0.4 | 2.1±0.0 | 0.75±0.07               |
| $ff_v = 10\%$ | Reference  | Front          | 11.02 ±0.21 | 750±5 | 65.1±1.0 | 5.4±0.4 | 0.77±0.06               |
|        | Rear         | 8.00±0.40      | 744±6   | 68.4±0.9 | 4.1±0.2 | 0.75±0.07               |
| $r = 100 \pm 15 \text{ nm}$ | Front | 12.70±0.60  | 761±1 | 63.2±1.1 | 6.1±0.1 | 0.77±0.06               |
|        | Rear         | 9.20±0.05      | 750±2   | 67.0±0.6 | 4.7±0.1 | 0.78±0.09               |
| $r = 135 \pm 15 \text{ nm}$ | Front | 12.96±0.14  | 762±4 | 64.4±1.4 | 6.4±0.1 | 0.78±0.09               |
|        | Rear         | 9.80±0.30      | 753±2   | 67.7±1.1 | 5.0±0.1 | 0.78±0.09               |
| $r = 200 \pm 25 \text{ nm}$ | Front | 13.54±0.12  | 769±7 | 64.3±0.5 | 6.7±0.1 | 0.80±0.11               |
|        | Rear         | 10.40±0.30     | 766±6   | 67.5±0.5 | 5.4±0.1 | 0.78±0.09               |

Table 1. Averaged photovoltaic parameters extracted from the $I$-$V$ curves of the devices with different scatterer filling fraction and radius of the scattering centres values. Data regarding reference cells and a cell integrating a back scattering layer were included.
systems including elements causing light scattering by means of Electrical Impedance Spectroscopy.\textsuperscript{51,52} Implementation of our approach has therefore no detrimental influence in the electrical properties of the devices.

A modification of the optical design implies a change in the spatial distribution of absorbed light within the electrode. We have calculated the light absorption profile, also known as electron generation function, in the active layer of a reference cell and of a cell including scatterers. Figure 5 shows the absorption per unit length along the z direction, defined in Fig. 1(b), in a 8-µm thick electrode of a reference cell under front, Fig. 5(a), and rear, Fig. 5(b), illumination, and that for a cell containing 160-nm radius spheres and \( f_r = 15\% \) under front, Fig. 5(c), and rear, Fig. 5(d), illumination. When comparing Fig. 5(c) with 5(a) and Fig. 5(d) with 5(b), we observe that light absorption is boosted in both cases, especially in the ca. 600 nm to ca. 750 nm range. Light harvesting is increased in regions close to the photoanode under front illumination, which might be a potential profit for devices in which the electron collection efficiency is low, as generation at distances closer to the contacts involves lower recombination probability.

**Conclusions**

We have developed a combined theoretical and experimental approach for the fabrication of efficient bifacial DSSCs through the random dispersion of spherical TiO\(_2\) scattering centres in their photoanode. As a consequence, absorption was boosted regardless of the illumination direction in the red part of the visible spectrum, where the absorption cross section of the commonly used N719 dye is low. Electric characterization of the devices revealed a significant enhancement of the \( J_{sc} \) value, and thus, efficiency both under front and rear illumination. The random nature of the approach makes the enhancement independent on the direction of illumination of incoming light, which is evidenced by the high rear to front efficiency ratio values. Using only standard cell components, and playing only with optical design, we were able to obtain values of the relevant photovoltaic parameters in line with those reported for state-of-the-art bifacial cells, which make use of at least 50% thicker electrodes than the ones herein considered and of modified counter electrodes. In this regard, the optically optimized working electrode herein proposed is compatible with any complementary method for performance improvement under rear illumination. Our approach may be applied to the fabrication of other systems in which finely-tuned disorder may result advantageous, offering thus potential benefits for the development of optoelectronic devices for which an accurate control of light absorption and emission is desired.

**Acknowledgements**

Funding for the development of the research leading to these results was received from the European Research Council under the European Union’s Seventh Framework Programme (FP7/2007-2013)/ERC grant agreement n°307081 (POLIGHT) and the Spanish Ministry of Economy and Competitiveness under grant MAT2014-54852-R. JMMM acknowledges the Spanish Ministry of Education, Culture and Sport for the funding through an FPU program. AJS thanks Spanish Ministry of Economy for funding through an FPI program under the project MAT2011-23593. YL acknowledges the funding from the People Programme (Marie Curie Actions) of the European Union’s Seventh Framework Programme FP7/2007-2013/ under REA grant agreement n° 622533.
5 R. Kern, N. van der Burg, G. Chmiel, J. Ferber, G. Hasenhindl, A. Hinsch, R. Kinderman, J. Kroon, A. Meyer, T. Meyer, R. Niepmann, J. van Roosmalen, C. Schill, P. Sommeling, M. Späth and I. Uhlendorf, Opto-Electron Rev., 2000, 8, 284.
6 A. Hinsch, J. M. Kroon, R. Kern, I. Uhlendorf, J. Holzbock, A. Meyer and J. Ferber, Prog. Photovolt., 2001, 9, 425.
7 A. Kay and M. Grätzel, Sol. Energ. Mater. Sol. C, 1996, 44, 99.
8 A. Fakharuddin, R. Jose, T. M. Brown, F. Fabregat-Santiago and J. Bisquert, Energy Environ. Sci., 2014, 7, 3952.
9 A. Hübner, A. G. Aberle and R. Hezel, Appl. Phys. Lett., 1997, 70, 1008.
10 S. Ito, S. M. Zakeeruddin, P. Comte, P. Liska, D. Kuang and M. Grätzel, Nat. Photonics, 2008, 2, 693.
11 J. X. Dang, J. Qi, M. T. Klug, P. Chen, D. S. Yun, N. X. Fang, P. T. Hammond and A. M. Belcher, Nano Lett., 2011, 11, 3795.
12 J. Liu, Q. Tang, B. He, L. Liu, H. Han, Chem. Phys. Chem., 2012, 14, 14383.
13 Y. Rong, Z. Xu, X. Li and H. Han, J. Mater. Sci., 2015, 50, 3803.
14 H. Cai, Q. Tang, B. He, R. Li and L. Yu, Nanoscale, 2014, 6, 15127.
15 Y. Duan, Q. Tang, J. Liu, B. He and L. Yu, Angew. Chem. Int. Ed., 2014, 53, 14569.
16 Y. Duan, Q. Tang, B. He, R. Li and L. Yu, Nanoscale, 2014, 6, 12601.
17 J. Liu, Q. Tang, B. He and L. Yu, J. Power Sources, 2015, 275, 288.
18 D. Song, M. Li, Y. Li, X. Zhao, B. Jiang and Y. Jiang, ACS Appl. Mater. Interfaces, 2014, 6, 7126.
19 Q. Tai, B. Chen, F. Guo, S. Xu, H. Hu, B. Sebo and X. Zhao, ACS Nano, 2011, 5, 3795.
20 J. Wu, Y. Li, Q. Tang, G. Yue, J. Lin, M. Huang and L. Meng, Sci. Reps., 2014, 4, 4028.
21 S. Xu, Y. Luo, G. Liu, G. Qiao, W. Zhong, Z. Xiao, Y. Luo and H. Ou, Electrochim. Acta, 2015, 156, 20.
22 H. Zhang, B. He, Q. Tang and L. Yu, J. Power Sources, 2015, 275, 489.
23 N. Fu, Y. Fang, Y. Duan, X. Zhou, X. Xiao and Y. Lin, ACS Nano, 2012, 6, 9596.
24 N. C. Jeong, C. Prasittichai and J. T. Hupp, Langmuir, 2011, 27, 14609.
25 X. Dang, J. Qi, M. T. Klug, P. Chen, D. S. Yun, N. X. Fang, P. T. Hammond and A. M. Belcher, Nano Lett., 2013, 13, 637.
26 K. Guo, M. Li, X. Fang, X. Liu, B. Sebo, Y. Zhu, Z. Hu and X. Zhao, J. Power Sources, 2013, 230, 155.
27 S. Colodrero, A. Mihli, L. Häggman, M. Ocaña, G. Boschloo, A. Hagfeldt and H. Miguez, Adv. Mater., 2009, 21, 764.
28 J. Kim, J. K. Koh, B. Kim, J. H. Kim and E. Kim, Angew. Chem. Int. Ed., 2012, 51, 6864.
29 D. Baretta, A. Di Carlo, R. De Angelis, M. Casalboni and P. Prospisto, Opt. Express, 2012, 20, A888.
30 C. López-López, S. Colodrero, A. Jiménez-Solano, G. Lozano, R. Ortiz, M. E. Calvo and H. Miguez, Adv. Opt. Mater., 2014, 2, 879.
31 C. López-López, S. Colodrero and H. Miguez, Phys. Chem. Chem. Phys., 2013, 16, 663.
32 A. Usami, Chem. Phys. Lett., 1997, 277, 105.
33 M. Son, H. Seo, S. Kim, N. Hong, B. Kim, S. Park, K. Prabakar and H. Kim, Int. J. Photoen., 2012, 480929.
34 S. Hore, C. Vetter, R. Kern, H. Smit and A. Hinsch, Sol. Energ. Mater. Sol. C, 2005, 90, 1176.
35 H. Koo, J. Park, B. Yoo, K. Yoo, K. Kim and N. Park, Inorganica Chimica Acta, 2007, 361, 677.
36 Z. Wang, H. Kawauchi, T. Kashima and H. Arakawa, Coord. Chem. Rev., 2004, 248, 1381.
37 A. Usami, Sol. Energ. Mater. Sol. C, 2000, 64, 73.
38 J. Ferber and J. Luther, Sol. Energ. Mater. Sol. C, 1998, 54, 265.
39 F. E. Gálvez, E. Kemppainen, H. Miguez and J. Halme, J. Phys. Chem. C, 2012, 116, 11426.
40 Y. Chiba, A. Islam, Y. Watanabe, R. Komiya, N. Koide and L. Han, Jpn. J. Appl. Phys., 2006, 45, L638.
41 Y. Tachibana, K. Hara, K. Sayama and H. Arakawa, Chem. Mater., 2002, 14, 2527.
42 C. J. Barbé, F. Arendse, P. Comte, M. Jirousek, F. Lenzmann, V. Shklover and M. Grätzel, J. Am. Chem. Soc., 1997, 80, 3157.
43 S. H. Kang, J. Kim, H. S. Kim, H. Koh, J. Lee and Y. Sung, J. Photochem. Photobiol. A, 2008, 200, 294.
44 H. Arakawa, T. Yamaguchi, T. Sutou, Y. Koishi, N. Tobe, D. Matsumoto and T. Nagai, Curr. Appl. Phys., 2009, 10, 5157.
45 Y. Li, K. Yoo, D. Lee, J. Y. Kim, H. J. Son, J. H. Kim, C. Lee, H. Miguez and M. J. Ko, RSC Adv., 2015, 5, 76795.
46 G. Mie, Annalen der Physik, 1908, 330, 377.
47 I.W. Suidarta and P. Chylek, J. Opt. Soc. Am. A, 2001, 18, 1275.
48 G. Rothenberger, P. Comte and M. Grätzel, Sol. Energ. Mater. Sol. C, 1999, 58, 321.
49 F. E. Gálvez, P. R. F. Barnes, J. Halme and H. Miguez, Energy Environ. Sci., 2014, 7, 689.
50 Y. J. Kim, M. H. Lee, H. J. Kim, G. Lim, Y. S. Choi, N. Park, K. Kim and W. I. Lee, Adv. Mater., 2009, 21, 1.
51 G. Lee, H. Lee, M. Um and M. Kang, Bull. Korean Chem. Soc., 2012, 33, 3043.
52 J. Duranti, P. P. Boix, M. Gervaldo, G. M. Morales, L. Otero, J. Bisquert and E. M. Barea, J. Electroanal. Chem., 2012, 683, 43.