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**Introducing structural colour in DSCs by using photonic crystals: interplay between conversion efficiency and optical properties**

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Herein we analyze experimentally the effect that introducing highly reflecting photonic crystals, operating at different spectral ranges, has on the conversion efficiency of dye sensitized solar cells. The interplay between structural colour and cell performance is discussed on the basis of the modified spectral response of the photogenerated current observed and the optical characterization of the cells. We demonstrate that, with the approach herein discussed, it is possible to achieve relatively high efficiencies using thin electrodes while preserving transparency. At the same time, the appearance of the device can be controllably modified, which is of relevance for their potential application in building integrated photovoltaics (BIPV) as window modules.

**Broader context**

Dye sensitized solar cells attracted a great deal of attention in the early nineties as potentially relevant photovoltaic devices that could be used as window modules capable of converting light into electricity, due to their semi-transparency in the visible range. However, the need to boost their efficiency led to the use of optical designs based on diffuse scattering layers that rendered these solar cells opaque. In our work, we show that the efficiency of dye solar cells can be enhanced by coupling the light absorbing electrode to highly porous dielectric Bragg mirrors with photonic crystal properties, which improve the cell efficiency while preserving their transparency. Furthermore, the look of the device can be tailored to measure by integrating dielectric mirrors reflecting different colours, the interplay between colour and efficiency actually being one of the main objects of study in the work herein presented. For all these reasons, we believe the integration of photonic crystals in dye solar cells may lead to interesting developments in the field of building integrated photovoltaics.

**1 Introduction**

Since the early nineties, dye sensitized solar cells (DSCs)1,2 have attracted a great deal of attention due to the possibility of generating reasonable power conversion efficiencies at low manufacturing and environmental costs. These solar devices typically consist of a nanocrystalline wide band gap semiconductor, usually titanium oxide (TiO2), and a liquid redox electrolyte, typically based on a I−/I3− redox couple, in which the charge generation and transport processes take place. Light absorption occurs in sensitizer molecules attached to the surface of the semiconductor. The use of TiO2 nanocrystals not only yields a large active surface area for the dye molecules to be anchored to, but also guarantees the cell transparency in the visible region of the spectrum.

In recent years DSCs have reached an impressive efficiency record above 11%,3–5 which is the consequence of careful engineering of all the components that form the photovoltaic device. In this respect, some of the most relevant research routes have been focused mainly on the quest for more stable and highly efficient ruthenium sensitizers,4,6–8 the replacement of the volatile solvent in the liquid electrolyte9–12 or the use of different semiconductor oxide morphologies.13–15

Many of the attempts that have led to the most successful outcomes make use of strategies based on the use of diffuse scattering particles to increase the residence time of photons in the absorbing layer. Since multiple scattering caused by disordered particles is not spectrally selective in the regime usually employed in DSCs, the cell turns completely opaque. Keeping in mind that transparency is probably the most attractive feature of these devices for building integration, the search for different approaches to extend and enhance the light absorption capability of DSCs while keeping their transparency continues to be a major challenge in the field. In order to do so, designs of novel organic or metal free dyes displaying extraordinarily high molecular extinction coefficients16–19 that would also allow reducing the active layer thickness have been proposed in the last few years. Nevertheless, some of these systems still present limitations regarding narrow absorption bands and poor light harvesting in the red, which yield efficiencies somewhat below the values achieved with ruthenium complexes. Hence, alternatives that could improve the light harvesting efficiency (LHE) within the cell at certain wavelengths for which dye absorption is weak are currently required. In this respect, the integration of photonic structures with optical properties can lead to a fine control of light propagation within the photovoltaic device.20,21 By coupling both porous one and three-dimensional photonic crystals to the absorbing layer, significantly enhanced photocurrents and overall conversion efficiencies, when compared to a reference cell of the same thickness, have been observed.20,22–27 This effect arises from the reflection of non-absorbed photons back into the dyed electrode by the photonic crystal, which increases the chances of them being harvested by the cell. Unlike diffuse scattering layers, periodic photonic structures allow determination, with great precision, of the spectral range in which the optical absorption enhancement effect occurs. By limiting the enhancement effect to the range in which the dye absorbs, the semi-transparency of the cell is preserved.

The aim of this paper is to study the interplay between conversion efficiency and optical properties of recently reported DSCs integrating highly porous one-dimensional photonic crystals (1DPCs).28 Up to now, it has been experimentally demonstrated that this type of periodic lattice is able to act as a light harvesting enhancer, with results similar to the ones obtained with a diffuse scattering layer of a comparable thickness, but with a spectral selectiveness that allows preserving the device transparency. Herein, we show for the first time that it is possible not only to optimize the photocurrent enhancement of 1DPC based DSCs through a precise control of the optical properties of the implemented periodic lattices, such as the spectral position of the reflectance peak, but also to tune the cell appearance due to the combination of the photoactive layer absorption added to brilliant coloured reflections arising from the photonic structures. This feature could be of major interest for building integrated photovoltaics (BIPV) in which decorative aspects are also taken into consideration. In this work, the systematic increase in photovoltage for those cells in which the 1DPC has been integrated is also confirmed, which is attributed to the concomitant formation of a thin insulating layer on the TiO2 nanocrystals during the deposition of the photonic structure, as reported elsewhere.28,29 This synergic behaviour has yielded transparent cells of tunable colours with overall efficiency enhancements as high as 70% with respect to reference cells with active layers of the same thickness.

**2 Experimental section**

**Preparation of transparent photoelectrodes**

A transparent film made of 20 nm sized particle TiO2 paste (18-NRT, Dyesol®) was deposited by screen printing on top of the conductive FTO glass substrates (8 Ω cm−2, Pilkington®). After this, the working electrode was sintered at 525 °C for ½ hour, treated with an aqueous TiCl4 solution at 70 °C for 30 minutes and then sintered again at 525 °C. A 3 μm thick TiO2 layer was obtained for a deposited active area of 0.25 cm2, as checked using a Dektak® profiler. SiO2 and TiO2 nanoparticle suspensions with average sizes of 20 nm and 6 nm, respectively, were employed to build the 1DPC structure onto the TiO2 layer coated conductive glass. Whereas the former suspension was purchased from Dupont (34 wt% suspension in H2O, LUDOX® TMA), the latter one was synthesized using a procedure previously reported.30 The periodic lattice was then fabricated by stacking 8 alternate layers made of such nanoparticle suspensions using a spin coater (Laurell WS-400E-6NPP). Previously, both nanoparticle precursors were suspended in a mixture of water (21 vol%) and methanol (79 vol%); the lattice parameter of the periodic stack, that is the thickness of the unit cell, being modified by means of the rotation speed employed during the deposition process by spin-coating and/or the use of different concentrations of the nanoparticle precursor suspensions.31 In all cases, the TiO2 dispersion also contained a certain amount of polymer (PEG 20[thin space (1/6-em)]000, Fluka) following the weight relation of PEG[thin space (1/6-em)]:[thin space (1/6-em)]TiO2 = 0.5.28 Because of this, a thermal stabilization was necessary in order to avoid dissolving such layer after a subsequent deposition. This heat treatment was performed on a hot plate at 300 °C for 15 min and was repeated following every bilayer (SiO2/TiO2) deposition during the multilayer structure formation. After that, all samples were annealed at 450 °C for 30 min to remove organic remains and mechanically stabilize the entire structure.

**DSC assembly**

The set of samples prepared was immersed into a 0.2 mM dye solution (N719, Solaronix®) using ethanol as solvent for 5 hours. After the immersion they were rinsed with ethanol and dried at 60 °C for 5 minutes. Counter-electrodes were made by depositing colloidal platinum paste (PT1, Dyesol®) onto a conductive FTO glass substrate by screen printing and heating at 420 °C for 15 minutes. Both electrodes were sealed using a thermo-polymer (Surlyn 25, Solaronix®). The cells were finally filled with the liquid electrolyte through a hole made previously at the back of the platinized counter-electrode. The electrolyte composition was 100 mM I2 (Aldrich, 99.999%), 100 mM LiI (Aldrich, 99.9%), 600 mM [(C4H9)4N]I (Aldrich, 98%), and 500 mM 4-tert-butylpyridine (Aldrich, 99%), using 3-methoxy propionitrile (Fluka, ≥99%) as solvent. Then, the hole was sealed with a thermoplastic polymer and a glass cover slide.

**Optical characterization of photoelectrodes and DSCs**

Optical characterization was performed using a Fourier transform infrared spectrophotometer (BRUKER IFS-66) attached to a microscope and operating in reflection mode. A X4 objective with a numerical aperture of 0.1 (light cone angle ±5.7°) was used to irradiate the sample and collect the reflected light at quasi-normal incidence with respect to its surface. A spatial filter was used to selectively detect light from 1 mm2 circular regions of the sample. The refractive indexes and the thicknesses of the layers that form the multilayer stack were estimated by simulating the optical response obtained before sealing the cell with a model based on the scalar wave approximation.33 Optical transmission spectra were also measured with a UV-Visible spectrophotometer (UV-2101PC, Shimadzu Corporation).

**Photovoltaic characterization**

I–V characterization was carried out with a solar simulator (Sun 2000, Abet Technologies) including a 150 W xenon lamp and the appropriate filter for the correct simulation of the 1.5 AM G solar spectrum. The incident light power was corrected to be 100 mW cm−2 using calibrated silicon solar cells. I–V curves were obtained by applying an external bias to the cell and measuring the generated photocurrent with a digital source meter (Keithley 2400).

Incident photon to collected electron (IPCE) efficiency measurements were acquired using a home-built system composed of a 300 W xenon lamp, a monochromator with 1140 g mm−1 grating (Model 272, McPherson) controlled by a digital scan drive system (Model 789A-3, McPherson) and a picoammeter (Keithley 6485). A UV filter with a cut-off wavelength of 400 nm was used to remove second order harmonics exiting the monochromator. A silicon photodiode with calibration certificate (D8-Si-100 TO-8 Detector, Sphere Optics) was used to correct the cell response.

**3 Results**

A schematic design corresponding to a DSC in which a highly porous 1DPC has been integrated is displayed in Fig. 1. Such a periodic structure deposited onto the TiO2 active layer acts as a highly efficient back reflector that is able to partially localize photons of a certain wavelength range within the absorbing layer, therefore increasing their probability of optical absorption. At the same time, interconnected porosity permits the liquid electrolyte to flow through it without affecting the cell kinetics. Although the mechanism of light harvesting enhancement in these systems has been theoretically and experimentally demonstrated before,32 further optimization of the multilayer lattice has allowed achieving greater photocurrent increases that are on the order of the maximum theoretically predicted.33

Design of a DSC in which a highly porous 1DPC has been implemented. The multilayer structure acts as an efficient back reflector under front illumination conditions, thus increasing the probability of absorption of a certain wavelength range.

In order to study the interplay between structural colour and photovoltaic performance of DSCs, a set of TiO2 photoelectrodes integrating photonic structures that reflected different and well-defined wavelength ranges in the visible was prepared. These periodic lattices were characterized by the optical thickness of their unit cell Σinidi, where ni and di are the effective refractive index and the thickness of the layer made of nanoparticles of a specific composition. Nanocrystalline titania layers of 3 μm width were employed as supporting electrodes in all cases. Fig. 2a and b show the I–V characteristic curves of the cells measured under simulated sunlight radiation (100 mW cm−2, AM 1.5 G) and the corresponding IPCE efficiencies. For the sake of clarity, data corresponding only to those photonic crystal based cells showing a notably different response are presented. Results for a reference cell made of the same TiO2 layer thickness but without including any photonic structure are also shown. A large increment is attained for both short circuit photocurrent density (JSC) and open circuit photovoltage (VOC) for those samples in which the 1DPC has been implemented (Fig. 2a). Whereas the former effect originates at the higher light harvesting efficiency caused by the photonic crystal back reflection, the latter one seems to be a consequence of a conformal thin insulating coating deposited onto the nanocrystalline TiO2 surface during the multilayer building process.28,29 Also, it has been observed that this thin layer may also contribute to an increase of the photocurrent, although to a much lesser extent than the photonic structure. As a result of both contributions, increases in the overall performance up to 70% were achieved when compared to the reference cell. This result confirms that it is possible to reach photocurrent values similar to those attainable for much thicker electrodes without the adverse effect the latter ones can have on the cell photovoltage and fill factor (FF). On the other hand, the spectrally selective enhancement of light harvesting is also appreciable in the IPCE data acquired for the cells (Fig. 2b). It can be clearly seen that the spectral response generated by the DSC is greatly modified after the integration of periodic structures reflecting different wavelength ranges, a good agreement between the I–V and IPCE measurements being attained for different cells. In Fig. 2c, the respective transmittance spectra of the selected cells are plotted. It can be readily seen that the semitransparency of the cell is preserved after the introduction of the photonic multilayer. In those cases in which the optical Bragg maximum matches the longest wavelength side of the visible spectrum, an abrupt drop in transmittance is detected. For reflectors for which the photocurrent enhancement is larger, almost the same transparency spectral window is attained (see blue and green curves in Fig. 2a).

The effect of coupling different photonic crystals on cell transparency was also evaluated for the set of samples abovementioned according to standard methods commonly employed to determine light transmittance of solar radiation (τV) for glazing in buildings (ISO 9050:2003) and that make use of the following relation:



where V(λ) is the photopic spectral luminous efficiency function that represents the wavelength-dependent sensitivity for an observer in photometry (ISO/CIE 10527), Dλ corresponds to the AM 1.5 solar spectral irradiance and τ(λ) is the spectral transmittance of the sample. Whereas τV for the reference cell was around 40%, values comprised between 15 and 25% were estimated for the case of 1DPC based cells. In this case, the lowest τV is obtained for the cell in which the Bragg peak overlaps most of the human eye optical sensitivity curve. It is also important to mention that those values are close to 0% for DSCs including diffuse scattering layers to increase the device photocurrent.

Fig. 3 allows evaluation of the effect of the optical properties on the cell performance. In it, the increase in short circuit photocurrent density (ΔJSC) and the overall conversion efficiency (Δη) for samples with 1DPC with respect to the reference, as extracted from the I–V measurements, is shown for the whole set of samples prepared as a function of the 1DPC unit cell thickness. The different cell response, in terms of photogenerated current, is due to the coupling of photonic structures able to reflect different wavelength ranges back into the absorbing layer. It can be noticed that the maximum rise in photocurrent is attained after integrating a multilayer structure with a unit cell whose optical thickness is around 220 nm, which gives rise to a reflectance peak centred at 540 nm when measured within the complete cell. This result is in good agreement with previous theoretical calculations where the highest photocurrent enhancements, for the case of 3–4 μm electrodes, were obtained coupling 1DPCs whose Bragg peaks overlapped most of the absorption band of the ruthenium dye.31 Moreover, for the working electrode thickness herein considered, the less efficient systems are those corresponding to the integration of 1DPCs reflecting wavelength ranges above 650 nm, which corresponds to optical thicknesses of the unit cell comprised between 280 nm and 315 nm, and that also coincides with the range of very low absorption of the dye. For the extreme case in which the reflection is placed at 730 nm, the effect on the photocurrent is very small. Since variations of VOC and fill factor are approximately the same for all cells, Δη follows the same trend as ΔJSC. It is important to remark that the total thickness of these stacks is comprised between 500 nm and 900 nm, which is significantly thinner than the one usually employed for the diffuse scattering layer (around 4 μm), thus reducing possible charge recombination through the cell.

Due to the diverse optical reflectance of the integrated photonic crystals, a different spectral dependence of the photocurrent is expected for each one of the cells herein analyzed. A spectral enhancement factor, γ, was estimated as the ratio between the IPCE of the 1DPC based cells and that of the reference cell. To do so, the IPCE curves displayed in Fig. 2, corresponding to three periodic structures with a well differentiated optical response, were considered. The spectral behaviour of γ is plotted in Fig. 4. It can be observed that the spectral position at which the photocurrent enhancement peaks red-shift as the reflectance maximum does. For the case of the integration of the 1DPC reflecting shorter wavelengths (blue curve), a photocurrent increment (enhancement factor between 1.2 and 1.3) over a wider spectral range is also appreciable that does not correspond to photonic effects and that has been attributed to the effect of the thin insulating layer deposited onto the TiO2 nanocrystal surface.

Finally, we discuss the effect on the cell appearance caused by the introduction of this type of nanostructures within the device. Under rear illumination, the colour displayed by the cell is mainly due to the strong reflections arising from the photonic structure, except for that whose reflectance peak is located at shorter wavelengths (400 nm to 450 nm) and for which the overlap with the electrolyte absorption band should be taken into account. Under frontal illumination, however, light impinges first on the absorbing layer and then in the photonic crystal, whose reflectance served to further increase absorption. In this case, the wavelength range corresponding to the dye absorption band is abruptly suppressed in the frontal reflectance spectrum. This causes cells reflecting a clear blue and green colour from the rear side to present a completely different aspect when observed from the working electrode one. This asymmetric response of the cells observed under frontal (Fig. 5d–f) and rear (Fig. 5g–i) illumination conditions is noticeable by the naked eye, as seen in Fig. 5. Each pair of photographs (d and g, e and h, and f and i) correspond to the same cell photographed from the electrode and the counter-electrode side, respectively. Although some defects due to the presence of large particle aggregates that may form during the deposition process are observable in the pictures and could be responsible for diffuse scattering, specular reflectance measurements of the different photonic structures deposited onto the nanocrystalline electrode show an excellent agreement with the expected theoretical values calculated using the scalar wave approximation method.33 These observations prove that, without changing the sensitizer, a completely different look for dye solar cells can be achieved by means of introducing structural colour, preserving at the same time their transparency. All these features are of relevance for future applications in BIPV systems, since high overall performance devices could be attained with tailored illumination and decorative properties.

**4 Conclusions**

In this paper, we have analyzed the interplay between structural colour and efficiency in dye solar cells coupled to highly reflecting porous one-dimensional photonic crystals operating at different visible wavelength ranges. Increases in the overall performance up to 70% can be obtained due to both a photocurrent increment, caused by an optical absorption amplification over the spectral range in which the porous periodic nanostructure acts as a dielectric mirror, and a concomitant raise of the cell open circuit voltage. The effect the integration of these periodic structures has on the cell appearance both in reflection and transmission modes has also been studied; a strong dependence with the direction of illumination having been described. We have demonstrated both that transparency is preserved after integrating the photonic structure and that the colour reflected by the device can be tailored to measure by means of the parameters of the photonic nanostructure, which can be of major interest for applications in BIPV systems.

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**Figure captions**

Figure 1. Design of a DSC in which a highly porous 1DPC has been implemented. The multilayer structure acts as an efficient back reflector under front illumination conditions, thus increasing the probability of absorption of a certain wavelength range.

Figure 2. (a) I–V curves measured under standard illumination conditions (100 mW cm−2, AM 1.5 G) for DSCs coupled to different highly porous 1DPCs. The optical thicknesses of the unit cell employed for their construction are: 196 nm (blue line), 222 nm (green line) and 281 nm (red line). Results for a reference cell are also plotted for the sake of comparison (black line). A 3 μm thick active layer is used in all cases as supporting electrode. (b) Incident photon to collected electron (IPCE) efficiency measured for the samples abovementioned. (c) Transmittance spectra at normal incidence of the same set of cells (same colour code).

Figure 3. Photocurrent and conversion efficiency increment, ΔJSC (black diamonds) and Δη (grey circles), respectively, obtained after including different highly porous 1DPCs within DSCs as a function of the optical thickness of the unit cell employed for the construction of the photonic structure (bottom axis) and of the spectral position of the corresponding reflectance peak (top axis). The dotted line is a guide to the eye.

Figure 4. Photocurrent enhancement factor γ calculated from the IPCE measurements as the ratio between the IPCE of the 1DPC based cells and that of the reference cell. The optical thicknesses of the unit cell employed are: 196 nm (blue line), 222 nm (green line) and 281 nm (red line).

Figure 5. (a–c) Specular reflectance spectra measured for the 1DPC based cells under frontal (dotted line) and rear illumination conditions (solid line). The optical thicknesses of the unit cell employed are: 196 nm, 222 nm and 281 nm, respectively. The absorption of a dyed TiO2 layer of the same thickness is also plotted (brown line). (d–i) Pictures showing the colour displayed by the cell under different illumination conditions after coupling the abovementioned photonic structures. Left and right series of photographs were taken in reflection mode illumination from the electrode (d–f) and the counter-electrode (g–i) side, respectively.

Figure 1



Figure 2



Figure 3



Figure 4



Figure 5

