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1. Introduction

Solar energy is nowadays one of the most promising future energy resources due to the depletion of fossil fuels, which supply the major part of all energy consumed worldwide. Among the different types of solar cell technologies, dye sensitization of mesoporous oxide based films has attracted a great deal of interest in the last few years because of the possibility it offers to achieve moderate efficiency devices at very low cost, being therefore an interesting alternative to conventional p-n junction solar cells. Dye sensitized solar cells (DSSC) consist of a nanocrystalline wide band gap semiconductor (usually TiO$_2$) which is deposited onto a transparent conductive substrate, and on whose surface a dye is adsorbed. The cell is completed with a counterelectrode, and both electrodes are put into electrical contact by infiltrating a liquid electrolyte in between them. Light is absorbed by the dye and charges are separated at the interface between the dye and the metal oxide it is anchored to. The optimization of the conversion efficiency, that is the fraction of light intensity that is converted into electrical power, is a key issue for this type of solar systems. In this way, different modifications of the originally proposed cell have been made in order to improve its performance, most of them based on the use of different semiconductors, dyes or ionic conductor. There is also an increasing interest in employing nanostructures to improve solar energy conversion devices (Kamat, 2007).

Another interesting route to enhance the cell efficiency is to modify its optical design in order to improve the light harvesting efficiency (LHE) or absorptance within the cell. The approach that has been explored the most has been the use of a diffuse scattering layer made of large TiO$_2$ colloids that are either deposited onto the nanocrystalline electrode or mixed with the nanocrystalline titania (nc-TiO$_2$) slurry. In both cases, increase of the optical light path within the absorbing layer rises the matter-radiation interaction time thus enhancing the probability of photon absorption. It has to be bear in mind that any structure introduced in the cell must permit the electrical contact between the electrolyte and the sensitized semiconductor slab, which forces it to have a porosity capable of sustaining the flow of charges. In recent times, different alternatives to light management in DSSC are being proposed and realized due to the development of novel porous periodic photonic nanostructures that can be easily integrated in these devices. The aim of this chapter is to give a brief review of the efforts performed to improve the light harvesting in DSSCs.
through the optimization of their optical design and provide a detailed description of the new emerging possibilities based on coupling dye-sensitized electrodes to different periodic photonic nanostructures. It will be shown that they have a great potential for the manipulation of light propagation. A detailed description of the integration processes used, of the different mechanisms of light harvesting enhancement that take place, and of actual examples showing the improvement of performance achieved will be presented in this chapter.

2. Brief description of DSSC

Photovoltaic devices have become a promising alternative energy source in the last decades. They are expected to increasingly and significantly contribute to overall energy production over the coming years. The photovoltaic field, dominated mainly by inorganic solid-state junction cells, is now being challenged by the emergence of new devices based on nanocrystalline and conducting polymer films, which offer a very low-cost fabrication and attractive features such as transparency, flexibility, etc. that might facilitate the market entry. Among all of them, dye sensitized solar cells (DSSC) are devices that have shown to reach moderate efficiencies, thus being feasible competitors to conventional cells.

DSSC combine the optical absorption and charge-separation processes by the association of a sensitizer as light-absorbing material with a wide band-gap semiconductor (usually titanium dioxide). As early as the 1970s, it was found that titanium dioxide (TiO$_2$) from photoelectrochemical cells could split water with a small bias voltage when exposed to light (Fujishima & Honda, 1972). However, due to the large band-gap for TiO$_2$, which makes it transparent for visible light, the conversion efficiency was low when using the sun as illumination source. Dye sensitization of semiconductor electrodes dates to the 1960s (Gerischer & Tributsch, 1968). This pioneering research involved an absorption range extension of the system into the visible region, as well as the verification of the operating mechanism by injection of electrons from photoexcited dye molecules into the conduction band of the n-type semiconductor. Since only a monolayer of adsorbed dye molecules was photoactive, light absorption was low and limited when flat surfaces of the semiconductor electrode were employed. This inconvenience was solved by introducing polycrystalline TiO$_2$ (anatase) films with a surface roughness factor of several hundreds (Desilvestro et al., 1985; Vlachopoulos et al., 1988). The amount of adsorbed dye was increased even further by using mesoporous electrodes, providing a huge active surface area thereby, and cells combining such electrodes and a redox electrolyte based on iodide/triiodide couple yielded 7% conversion efficiencies in 1991 (O’Regan & Gratzel, 1991). The current highest energy conversion efficiency is over 11% (Chiba et al., 2006), and further increase of the efficiency is possible by designing proper electrodes and sensitization dyes.

Figure 1 shows both a scheme and an energy level diagram of a liquid electrolyte dye sensitized solar cell. They usually consist of one electrode made of a layer of a few micrometers of titanium dioxide nanocrystals (average crystal size around 20 nm), that have been sintered together to allow electronic conduction to take place. A monolayer of a sensitizer dye, typically a ruthenium polypyridyl complex, is attached to the surface of the nanocrystalline electrode. This mesoporous film is deposited onto a conductive, transparent substrate, typically indium tin oxide (ITO) or fluorinated SnO$_2$ (FTO), and soaked with a redox electrolyte, typically containing I$_3^-$/I$^-$_3 ion pairs. This electrolyte is also in contact with a colloidal platinum catalyst coated counter-electrode. Sunlight is harvested by the dye producing photo-excited electrons that are injected into the conduction band of the
nanocrystalline semiconductor network, and then into the conducting substrate. At the same time the redox electrolyte reduces the oxidized dye and transports the electron acceptors species (I$_3^-$) to the counter-electrode, where the I$_3^-$ is reduced back to I$^-$ and the electrical circuit is completed via electron migration through the external load.

Fig. 1. Cross section view of the design of a dye sensitized solar cell under illumination conditions (left), and energy levels of the different components of the cell that represent the energetics of operation of such devices (right).

In contrast to silicon devices, charge separation is primarily driven by the oxidation/reduction potentials of the different species at the TiO$_2$/dye/electrolyte interface, being screened out any electric field gradient in the TiO$_2$ electrode due to the high concentration of mobile ions employed in the liquid electrolyte (Zaban et al., 1997). Photoinduced charge separation takes place at the TiO$_2$/electrolyte interface. Thus, electron injection requires the dye excited state to be more reducing than the TiO$_2$ conduction band. In the same way, regeneration of the dye ground state by the redox couple requires the dye cation to be more oxidizing than the I$^-$/I$_3^-$ redox couple (Mori & Yanagida, 2006). The voltage output of the device is approximately given by the splitting between the TiO$_2$ Fermi level and the chemical potential of the redox electrolyte, being the former related with the density of injected electrons and the density of charge traps in the band gap of TiO$_2$. Under illumination conditions, the density of electrons injected into the semiconductor conduction band increases, raising the Fermi level towards the conduction-band edge and generating a photovoltage in the external circuit.

Charge transport processes within the cell are considered to be diffusive (Södergren et al., 1994), (Cao et al., 1996), (Schwarzburg & Willig, 1999) and are driven by concentration gradients generated in the device, thus making electrons to go towards the working electrode and triiodide ions towards the counter electrode. During the diffusion process, photogenerated electrons can recombine with acceptors species, such as dye cations and triiodide ions. Another loss pathway includes decay of the dye excited state to ground (Huang et al., 1997), (Nelson et al., 2001). Kinetic competitions between the different forward and loss pathways are therefore critical to determine the quantum efficiencies of charge separation and collection, and so the conversion efficiency. A diagram showing the kinetics of a DSSC is presented in Figure 2. It should be noticed that not only energetics but also
kinetics must be taken into account, and they constitute the key issues to achieve high energy conversion devices.

Fig. 2. Kinetics and competitive processes involved in the conversion of light to electric power in DSSC.

The overall conversion efficiency ($\eta$) of the dye-sensitized solar cell is determined by the photocurrent density measured at short circuit ($J_{SC}$), the open-circuit photovoltage ($V_{OC}$), the fill factor (ff), and the power of the incident light ($P_{in}$). These values can be extracted from the photocurrent density-voltage characteristics (IV curves) under AM 1.5 full sunlight ($P_{in}=100$ mWcm$^{-2}$). The relation between $J$ and $V$ is determined by varying the resistance of the outer circuit, being $J_{SC}$ obtained when the resistance of the outer circuit is zero (thus voltage is zero) and $V_{OC}$ when the resistance is maximum (thus photocurrent is zero). The output power of the device equals the product of $J$ and $V$, and the fill factor expresses the efficiency of the device compared to that of an ideal cell. $P_{max}$ is commonly reported as the output power of the commercial device and corresponds to the maximum value that can reach the output power. The performance of DSSC can be therefore estimated using the following equations:

$$\eta(\%) = \frac{J_{SC} \cdot V_{OC} \cdot ff}{P_{in}}$$

Where,

$$ff = \frac{P_{max}}{J_{SC} \cdot V_{OC}}$$

A typical IV curve corresponding to a 7 µm thick dyed-TiO$_2$ electrode measured under 1 sun illumination is displayed in Figure 3 (left). The solar radiation and the ruthenium dye absorptance spectra are shown in Figure 3 (right).

For a detailed description of DSSCs, we refer the reader to M. Graetzel (Graetzel, 2000) and M. Graetzel and J. Durrant (Graetzel & Durrant, 2008).

In the next section, we analyze two different approaches that contribute to the enhancement of DSSC efficiencies through the control of photon absorption into the cell. We put special emphasis to describe the integration of new materials known as porous one-dimensional photonic crystal due to their ease of integration and demonstrated promising performance.
Fig. 3. IV curve for a 7 µm thick TiO$_2$ electrode, for which N719 as dye and a I$_{-}$/I$_{3}^{-}$ redox couple based liquid electrolyte have been employed (left), and mismatch between the dye absorption spectrum and that for the AM 1.5 solar spectrum (right).

### 3. Approaches to light management in DSSC

In the last years, many attempts using different modifications of the originally proposed cell have been made in order to improve its performance, most of them based on the use of different semiconductors (Tennakone et al., 1999), dyes (Wang et al., 2005) or ionic conductors (Wang et al., 2004). However, the extremely delicate sensibility of the charge transport and recombination dynamics to any alteration of the nature of the interfaces present in the cell should be considered (Haque et al., 2005). For instance, some of the most important routes of research have focused on the molecular engineering of suitable dyes having broader absorption spectra that show a better matching to the solar spectrum and higher molar extinction coefficients (Wang et al., 2005), thus yielding higher short circuit currents. However, further improvements in terms of cell stability and durability should be done. On this respect, the performance of cells using solid state hole conductor based DSSC (Bach et al., 1998) to increase the long-term stability still remains far from that achievable when liquid organic electrolytes are employed.

The quantification of the electrical kinetic parameters of the cell has attracted the attention of many research groups and a great effort has been made in this direction. However, less interest has been paid to the study and development of optical elements that could be introduced in the cell for boosting the optical path of light, thus increasing the probability for the photons to be absorbed. Although it was well-known that by optical means the output power of the cell can be enhanced through a higher photogenerated current, since it depends on the number of photons collected by the dye (Tachibana et al., 2002), it was also clear that the introduction of optical elements that can enhance light harvesting in DSSC was not straightforward. First, they are typically made of dense materials, which would block the flow of charged species in solution. Second, the standard fabrication and integration processes usually employed to make optical materials did not seem to be compatible with the colloidal chemistry approaches normally taken to prepare a DSSC. The first and most successful approach to light management in DSSC was based on the introduction of a diffuse scattering layer, as described below, which largely enhances the photon path length through the working electrode, thus increasing the probability of optical absorption to take
place. More recently, approaches based on periodic structures are also being investigated with promising results. Apart from the large enhancements of efficiency these latter structures gives rise to, they present the added advantage of allowing for the precise selection of the spectral range at which optical absorption is amplified, leading to both control over the aspect and the semi-transparency of the cell.

3.1 Effect of increase optical absorptance on the efficiency of the cell

Optical approaches to raise $J_{SC}$ and therefore efficiencies, are based on the increase of optical absorption caused by either an enlargement of the photon path length through the working electrode or light trapping effects occurring within the TiO$_2$ electrodes. $J_{SC}$ can be attained by integrating the product of the ratio between the solar spectral irradiance and the photon energy density, $F(\lambda)$, and the photon-to-current conversion efficiency, IPCE, of the cell over the wavelength of the incident light:

$$J_{SC} = \int_\lambda q\xi(\lambda)F(\lambda)\text{IPCE}(\lambda)d\lambda$$

Here $q$ is the electron charge and $\xi(\lambda)$ is a factor that accounts for the losses at the air-substrate interface. IPCE can be expressed as the product of light harvesting efficiency (LHE) and the electron-transfer yield $\Phi(\lambda)$, that is the product of the electron injection yield and the charge collection efficiency.

$$\text{IPCE}(\lambda) = \text{LHE}(\lambda)\Phi(\lambda)$$

The LHE or optical absorptance, $A$, at a certain wavelength is defined as the fraction of incident photons that are absorbed by the dyed electrode: $A = I_A/I_0$, where $I_0$ is the incident intensity and $I_A$ the intensity absorbed. Therefore the relationship between LHE and $J_{SC}$ is given by the expression:

$$J_{SC} = \int_\lambda q\xi(\lambda)F(\lambda)\text{LHE}(\lambda)\Phi(\lambda)d\lambda$$

In a first approximation, absorptance for a standard dyed electrode is related with the extinction coefficient and the concentration of the dye. Since only a monolayer of dye molecules is attached to the surface of the TiO$_2$ nanoparticles, its total amount is directly related to the oxide layer thickness. For example, a 7 $\mu$m thick dye sensitized (N719) mesoscopic electrode can absorb nearly the 80% of incident photons at the maximum absorption wavelength. However, photons still in the visible range but of lower energy are weakly absorbed. Looking for a dye absorption enhancement, devices having thicker electrodes (around 10 $\mu$m) have been previously reported (Ito et al, 2006). Nevertheless, the thickness of TiO$_2$ layer cannot be increased at will without affecting its mechanical properties, reaching mass transport limitations in the electrolyte or and reducing the photovoltage of the cell. In addition, electrons injected in the conduction band must travel a longer distance to reach the back contact, increasing the probability of recombination at grain boundaries and diminishing both current and voltage of the cell, as experimentally demonstrated (Ito et al., 2008). Finally, another disadvantage to scale-up the device would appear due to the high cost of sensitizer dyes (approx. 1000€/g). The thicker the electrodes, the higher the dye loads required, therefore raising the final cost of the DSSC. All these non-
desirable features make it preferable to increase the absorption of the cell for a given dye and film thickness, modifying the optical path length within the film and improving the spectral response of the photoelectrode. Keeping in mind that a standard dye sensitized layer of around 7-8 μm thick will not absorb light strongly, these achievements can be obtained by reflecting light back to the dyed electrode. In what follows, we provide an overview of the different approaches taken towards the integration of optical passive components in order to increase the power conversion efficiency of DSSCs.

3.2 Diffuse scattering layer

TiO$_2$ working electrodes used in DSSC are composed of 20 nm size crystallites. These electrodes are essentially transparent since visible light is not scattered for titania particles of sizes on the order of the few tens of nanometers. In fact, the incident photons that are not absorbed by the dye sensitized electrode are either lost through the counter electrode or partially absorbed by the electrolyte solution. From a photo-chemical point of view, this implies that part of the reagent (light) is wasted. The first attempt to collect these escaping photons were based on the use of polydisperse packings of sub-micron size spheres as highly diffusive reflecting layers (see figure 4). The intensity of the scattering effect depends on the size and refractive index of the particles as well as on the refractive index of the medium surrounding them. Hence, particle sizes between 300 nm and 1000 nm made of transition metal oxides with high refractive index, such as TiO$_2$ (rutile $n=2.8$ or anatase, $n=2.4$) or ZrO$_2$ ($n=2.1$) can be used as efficient scatterers. The introduction of a reflecting layer in DSSC to scatter photons and re-inject them into the electrode was proposed in a theoretical work by Usami (Usami, 1997). In other attempt, Ferber and Luther simulated the scattering process for a mixture of small and large particles, concluding that an enhancement in photon absorption was produced (Ferber & Luther, 1998). Subsequent simulations using different approaches were made (Rothenberger et al., 1999), for which a 6% of increase of the photon flux was predicted.

The integration of scattering centre particles in DSSC can be experimentally done under different architectures. In one approach, they are jointly included with the TiO$_2$ nanocrystallites that form the electrode (Tachibana et al., 2002). In another, they are deposited as a second layer on top of the dye sensitized electrode in a well-known configuration referred to as “double-layer” (Hore et al., 2006). The latter configuration is normally the most employed. Other ways of integrating scattering layers made of submicron size disordered particles have also been reported (Wang et al., 2004), (Zhang et al., 2007). In general, the scattering layer is deposited using methods similar to those used for the TiO$_2$ electrode deposition, such as doctor blade, screen printing, etc. A porous network connection between both layers is needed to allow the dye load and a proper diffusion of the charge carriers.

Improvements of efficiency around 20% in average are reported using the arrangements before described for nc-TiO$_2$ layers with thicknesses between 5 and 7 microns. In fact, the efficiency record attained for a DSSC corresponds to a cell that incorporates a highly scattering layer (Chiba et al., 2006). The boost in efficiency is mainly a consequence of the increase of $J_{SC}$ up to 20%. On the other hand, IPCE values can be incremented between 20% and 50% depending on the spectral region considered. The highest improvement is obtained in the red part of the spectrum, where the dye extinction coefficient is small. Additionally, this light-scattering layer has been shown to act not only as a photon-trapping system but also to be an equally active layer in photovoltaic generation (Zhang et al., 2007).
The disadvantage of employing diffuse light scattering layers or mixed light scattering particles in DSSC is the loss of transparency of the cell. Unfortunately, the cells turn opaque, leaving them useless as window modules or any other application where transparency, one of the added values of these cells, was required. Also, the thickness of the electrode largely increases, particularly in the case of the double layer configuration, which might cause an increase of the resistance of the cell and a reduction of the voltage.

### 3.3 Periodic structures

An alternative to the use of disordered structures to enhance diffuse light scattering is the introduction of porous materials in which a periodic variation of the refractive index has been built up. As it will be shown next, periodic structures allows to achieve high reflectance within the cell at targeted and well-defined wavelength ranges, which may prevent the drawback of the loss of transparency. Also, in some cases, highly reflecting structures can be only a few hundreds of nanometres thick, which reduces the potential problems of increase of resistance and reduction of the photovoltage. Depending on the spatial dimensions where the modulation of refractive index is found, we will refer these structures as one, two, or three dimensional photonic crystals (1DPC, 2DPC, or 3DPC, respectively) (Joannopoulos et al. 1995). The interference effects associated with these periodic dielectrics give rise to the opening of a photonic band gap whose effect is detected as a maximum in the specular reflectance spectrum of the structure. In the following section, the effect of integrating both 3DPC and 1DPC in DSSC is described.

#### 3.3.1 Three dimensional ordered structures

In 2003, Mallouk and co-workers proposed the use of a novel type of optical elements to improve the efficiency of DSSC. Their approach was based on the coupling of a particular type of 3DPC to dye-sensitized nc-TiO$_2$ films (Nishimura et al., 2003). This approach consisted of integrating a 3 μm layer of a TiO$_2$ ordered porous structure, known as inverse opal (see figure 5). By doing so, IPCE was shown to increase with respect to that of a standard cell used as reference (Figure 6a). Although the origin of this enhancement was first attributed to the reduction of the group velocity of photons near the edge of a stop band or photonic pseudogap, which implies the increase of the probability of absorption, it was later found that the absorption enhancement effect was partly due to the diffuse scattering...
caused by the imperfections present in the opal film (Halaoui et al., 2005) and, mainly, to the coupling between a standard electrode and the ordered structure, as explained next.

![Image](https://example.com/image1.png)

**Fig. 5.** (a) SEM cross section image of an inverse TiO$_2$ opal. 300 nm latex spheres were used as template, and then removed by thermal treatment. (b) Scheme and (c) SEM cross section image of a TiO$_2$ 3D inverse opal deposited on top of a TiO$_2$ nanocrystalline electrode.

The theoretical analysis of the phenomena (Mihi & Míguez, 2005) demonstrated that the enhancement of the photocurrent in bilayer structures formed by a dye sensitized nanocrystalline TiO$_2$ film coupled to an inverse titania opal is mainly due to the surface resonant modes confined within the overlayer (figure 6b). This is a consequence of the mirror effect of the photonic crystal. The theoretical results identified an increase in the absorptance spectrum of the modelled bilayer and an estimated photocurrent enhancement factor very similar to that reported in Mallouk experiments (Figure 6c). Later experimental results confirmed convincingly the model proposed by Mihi & Míguez (Lee et al., 2008; Mihi et al., 2008) and as they predicted, the improvement was found for frequencies comprised within the photonic pseudogap of the inverse opal structure. In that way, the dependence of the increased IPCE with the position of the forbidden interval range can be employed to enhance absorption at desired spectral ranges. The selection of this region is made through the lattice parameter of the photonic crystal which is controlled as well by the size of the templating spheres and the infiltration degree. In these specific experiments, DSSC required an opal with a lattice parameter that gives red photocurrent enhancement. Additionally it is possible to couple two or more 3DPC with different lattice parameters to enhance photocurrent in a wider spectral range (Mihi et al., 2006). Since this effect was confirmed theoretically, we can mention that the disadvantage of these materials is the several steps involved to achieve these types of structures. This leads to defects within the 3D photonic crystal, and therefore a lower reflectivity is obtained.

### 3.3.2 DSSC coupled to 1DPC

Although the coupling of inverse opals to dye sensitized electrodes demonstrated an increased IPCE with respect to that of a reference cell (Nishimura et al., 2003), the main drawback of these 3D structures is the difficult assembly process to achieve reasonable reflecting periodic materials, which leads usually to thick structures (between 5-10 micron thick). This might have a deleterious effect on charge transport and recombination through the cell. Very recently, new types of one-dimensional photonic crystals (1DPC) have been prepared by alternate deposition of either mesoporous (Choi et al., 2006); (Fuertes et al., 2007) or nanoparticles (Wu et al., 2007); (Colodrero et al., 2008) based films. These structures
Fig. 6. (a) Circles: Photogenerated current observed for a bilayer DSSC like the one shown in the inset when illuminated from the rear side. Squares: Photocurrent corresponding to a non periodically structured, standard DSSC. These data have been extracted from Nishimura et al., 2004. The curve in (b) shows the calculated absorptance (or LHE) for the structure shown in the inset under rear illumination. (c) Averaged absorptance of bilayer DSSCs formed by nc-TiO$_2$ inverse opals of different width (from 3 to 17 sphere monolayers), each one of them having in turn different nc-TiO$_2$ layer thickness on top (from 6.5 $\mu$m to 7.5 $\mu$m). Dotted lines in (b) and (c) are the calculated absorptance spectra of standard DSSC having the same amount of absorbing material than in the bilayer system. The insets show schemes of the modelled structure. The corresponding illumination direction is indicated by an arrow.

(Extracted with permission from Mihí & Míguez, 2005)

are usually easier to build and integrate than those abovementioned of higher dimensionality and present attractive features, such as very intense and wide Bragg reflections and reduced thickness (less than a micron versus the several micron thickness of opals). Furthermore, the advantage of such lattices lies on the wide range of materials available to be deposited as multilayers, which implies accurate control over the optical properties of the periodic ensemble, and on the high structural and optical quality attainable. These nanostructures could therefore be a potentially interesting alternative to other type of light scattering layers used within the solar cell field, having created high expectations due to the large improvement of the performance achieved for this type of devices.

In this section, we will focus on mesostructured Bragg reflectors in which the building blocks are nanoparticles of different sort (Colodrero et al., 2008) that can be easily coupled to DSSC to enhance the optical absorption. The novelty of these nanostructures is mainly the large and highly accessible interconnected mesoscopic porosity that they can present, which makes them suitable for this type of solar devices. In fact, some of the most successful
approaches developed to improve the LHE in silicon photovoltaic systems are based on the implementation of coherent scattering devices such as highly reflecting distributed Bragg reflectors (Johnson et al., 2005), surface gratings (Llopis & Tobias, 2005), or a combination of both (Zeng et al., 2006). However, the implementation of such structures in DSSC had been no possible due to the need for porous back reflectors that allowed a proper flow of the electrolyte through the cell and, at the same time, due to the complicated deposition process of solid layers from colloidal suspensions.

The fabrication of DSSC containing nanoparticle based 1DPC involves two basic steps: first, the deposition of the nanocrystalline TiO$_2$ layer that acts as electrode onto a transparent conducting substrate, and second, the stacking of layers made of nanoparticles of different kind deposited alternately by spin-coating onto the sintered electrode. In this case, silica and titanium dioxide suspensions are employed because of the very high refractive index contrast they present, which allows achieving broad and intense Bragg reflections. The nanoparticle multilayer is periodic with a period of around a hundred nanometers, the thickness of these layers being controlled through either the concentration of the precursor suspensions or the rotation speed of the substrate during the spin coating process. Figure 7 shows a scheme of the described 1DPC based cell, as well as FESEM images corresponding to a cross section of both the nanocrystalline-TiO$_2$ electrode and the periodic structure deposited onto the former. The uniformity in the thickness of both types of layers composing the 1DPC, and even the different morphology of the particles employed, can be clearly distinguished in the picture below. The total thickness of the photonic crystal can vary between 0.5 to less than 2 microns, depending mainly on the lattice parameter of the structure and the number of layers that compose the periodic stack.

Fig. 7. Left: Design of a DSSC coupled to a nanoparticle based 1DPC. Right: FESEM images showing the TiO$_2$ nanocrystals forming the solar cell electrode (top), on which the porous periodic stack made of nanoparticles of different kind is deposited (bottom). In this case, a six layer photonic crystal has been implemented.

The procedure that follows to complete the solar cell is the same than the one usually employed for standard DSSC. It should be noticed that the nanoparticle multilayer integrated into the solar cell in this way behaves as a distributed Bragg reflector, providing the cell with a brilliant metallic reflection whose colour can be tuned by varying the thickness of the layers forming the periodic nanostructure. This can be readily seen in the photographs shown in Figure 8, in which the appearance of a reference cell and the same
cell including two different 1DPC under perpendicular illumination are shown. Another remarkable issue from these systems is that the multilayer implemented like that does not alter significantly the cell semi-transparency, contrary to what happens when other scattering layers made of large titania nanoparticles are employed in DSSC to increase the photogenerated current. When these diffuse scattering layers are used, the solar cell becomes almost completely opaque as a consequence of the lack of spectral selectiveness of the incoherent scattering by slurries with a wide particle-size distribution. The comparison between the optical transmission spectra for the case of a standard reference cell (7.5 micron thick) and those corresponding to solar cells possessing the same TiO$_2$ electrode thickness but coupled to different 1DPC and to a diffuse scattering layer are also included in Figure 8.

Fig. 8. Left: Images of a reference cell and different photonic crystal based DSSC. The brilliant colours displayed by the cell (bottom) arise from the periodic structures with different lattice parameter coupled to the dyed electrode (top image). Right: Transmittance spectra of a DSSC composed of a 7.5 micron thick electrode (black curve) and of the same electrode coupled to periodic structures with different lattice parameters (green and red curves). For comparison, the transmittance spectrum of a DSSC with the same electrode thickness but coupled to a 7.5 micron thick porous diffuse scattering layer is also plotted (black dashed line). (Extracted with permission from Colodrero et al., 2009 [b])

As explained in section 3.3.1, enhancement of optical absorption is primarily due to the partial localization of photons of certain narrow frequency ranges within the dyed TiO$_2$ electrode (that acts as absorbing layer) as a result of its coupling to the photonic crystal, which acts as a porous low-loss dielectric mirror (Mihi & Míguez, 2005). These optical modes could, in principle, be recognized as narrow dips in the reflectance spectra at frequencies located within the photonic band gap, the enhancement range being determined by the spectral width of the photonic band gap (Mihi et al., 2005). The first experimental demonstration of the mechanism of light harvesting enhancement that takes place in DSSC coupled to photonic crystals has been recently reported using the nanostructures under the scope of this section (Colodrero et al., 2009[a]). The effect of well defined optical absorption resonances was detected both in optical spectroscopy and photogenerated current experiments of very thin and uniform dye-sensitized TiO$_2$ electrodes coupled to high quality porous 1DPC, an unambiguous correspondence between them being established. This study demonstrated that light trapping within absorbing electrodes is responsible for the absorption enhancement that had previously been reported. Figure 9 shows the spectral
response of the IPCE for three DSSC having increasing electrode thicknesses range from 350 nm thick to 1.5 micron thick but the same 1DPC implemented. In each case, an enhancement factor $\gamma$ was calculated as the ratio between the IPCE of the 1DPC based cell and that of the reference one. The spectral behaviour of $\gamma$ for each cell is compared to its corresponding optical reflectance measured under front-side illumination. It can be clearly seen that peaks of photocurrent correspond to the dips in reflectance are obtained, which are the fingerprint of optical resonant modes localized in a film coupled to a photonic crystal.

For these modes, matter-radiation interaction times are much longer; thus, the probability of optical absorption, and therefore the photogenerated current, is enhanced. As the thickness of the dye-sensitized electrode increases, the number of localized modes rises and so does the number of peaks in the $\gamma$ curve. The presence of a photonic crystal not only enhances the photogenerated current but also allows one to vary the spectral photoelectric response of thin electrodes in a controlled manner. For instance, in the example shown in Figure 9a, the largest current is attained at $\lambda = 470$ nm instead of at $\lambda = 515$ nm, where the dye absorption curve reaches its maximum. Thus, the photonic crystal allows tailoring to measure the enhanced absorption window of the dye, and thus, its overlap with the solar spectrum.

![Fig. 9. Top: IPCE versus wavelength for cells containing the same 6 layer-1DPC coupled to dyed electrodes of increasing thicknesses in each case (from left to right). It is also plotted the IPCE for reference cells of the same electrode thickness without photonic crystal (blue circles). Bottom: Reflectance spectra of the 1DPC based solar cells (solid line) and the corresponding photocurrent enhancement factor (red circles). (Extracted with permission from Colodrero et al., 2009 [a])](https://www.intechopen.com)

On the other hand, besides the experimental demonstration and confirmation of the light harvesting enhancement mechanism achieved using 1DPC based solar cells, great improvements in power conversion efficiency ($\eta$) have also been observed in this type of solar devices coupled to highly reflecting nanostructures (Colodrero et al., 2009 [a]), (Colodrero et al., 2009 [b]). After analyzing the photocurrent density-voltage (J-V) curves under 1 sun illumination of DSSC, on which photonic crystals reflecting different ranges of wavelengths were coupled, it was found that the photocurrent was largely improved while
leaving the open-circuit voltage almost unaltered. The magnitude of this effect depends mainly on two factors: first, the spectral width and position of the photonic band gap relative to the absorption band of the ruthenium dye; second, the degree of optical coupling to the dye-sensitized electrode, which depends in turn on the thickness of that electrode. The magnitude of the photocurrent enhancement effect caused by the coupling to the 1DPC is therefore expected to be lower as the thickness of the electrode increases, since more photons are absorbed by the dyed nc-TiO$_2$ layer when they first pass through it. For this case, red reflecting 1DPCs might perform better, since the ruthenium dye captures less effectively solar radiation precisely for $\lambda$$>$600 nm. Results on the power conversion efficiency ($\eta$) for DSSC with a 7.5 micron thick electrode coupled to 1DPC reflecting different ranges of wavelengths (green and red) are shown in figure 10. An enhancement in the efficiency close to 20% with respect to that of the reference cell was obtained for the 1DPC based solar cell showing a better matching with the absorption spectrum of the dye.

Fig. 10. Left: IV curves of a 7.5 micron thick electrode coupled to different 1DPC under 1 sun illumination. The corresponding IV curve for a reference cell is also plotted (black line). Right: Reflectance spectra measured under frontal illumination conditions of the PC-based solar cells together with the absorption spectrum of the Ru-dye (arbitrary units).

The photocurrent enhancement reported using PC based solar cells could be even larger at lower incident radiation intensities, reaching up to 30% of the reference value under 0.1 sun for the samples above described. This is mainly due to the decrease of density of carriers when so does the incident light intensity, which has a positive effect on electron transport and recombination through the cell. Besides, any resistance potentially introduced by the photonic crystal will have a minor effect at lower illumination conditions, since its effect increases with the number of carriers. In order to illustrate this effect, values of efficiency, photogenerated current and open-circuit voltage obtained for DSSC having 7.5 micron thick electrodes coupled to different 1DPC are presented in Figure 11. The variation of $J_{sc}$ and $V_{oc}$ with intensity of the incident radiation confirms that the presence of the PC enhances the photocurrent significantly, but has a minor effect on the photovoltage. The linear and logarithmic dependence observed for $J_{sc}$ and $V_{oc}$, respectively, versus incident radiation
intensity are in good agreement with theoretical predictions (Nazeerudin et al., 1993; Södergren et al., 1994).

To conclude this section and in order to prove the performance of these nanoparticle based structures as light harvesters, DSSC based on both 1DPC and diffuse scattering layers were evaluated and compared. For this purpose, a 7.5 micron diffuse scattering layer made of titania spheres 130 nm in diameter mixed with a paste similar to that employed to prepare the nanocrystalline titania layer was deposited onto a 7 micron thick reference electrode. A similar electrode was coupled to a 700 nm thick highly reflecting 1DPC. In order to perform a comparison of the effect on light harvesting these different architectures have, the 7 micron thick diffuse scattering layer was electrically isolated from the dye-sensitized electrode by introducing a thin layer of silica spheres 30 nm in diameter between them. By doing so, no contribution to the photocurrent from the different scattering layers employed is measured, since the 1DPC is also based on alternate layers of SiO$_2$ and TiO$_2$ nanoparticles, the first layer deposited onto the electrode being insulating. The effect of the PC on the short circuit photocurrent is observed to be similar and comparable to that of a diffuse scattering layer, provided that a suitable PC is chosen, as displayed in figure 12. Furthermore, the open circuit voltage is slightly higher in the case of the PC, which might be due to its much smaller width. It should be reminded that the enhancement in the case of PC is based on the partial confinement of light of a selected frequency range within the absorbing electrode, whereas in the case of diffuse scattering layers, the increase in efficiency is based on the random and non-selective scattering of visible light in all directions.

Fig. 11. Efficiency ($\eta$), short-circuit current density ($J_{sc}$) and open-circuit voltage ($V_{oc}$) for a reference cell (open black circles) and for those PC based cells having the same electrode thickness coupled to 1DPC with different lattice parameters (green and red symbols) under illumination at different light intensities. (Extracted with permission from Colodrero et al., 2009 [b])
Fig. 12. Comparison between the efficiencies for a DSSC made of a 7 micron thick electrode and those corresponding to the same electrode thickness coupled to a diffuse scattering layer and a 1DPC. The thicknesses employed for the diffuse scattering layer and the periodic structure are 7.5 micron and 700 nm, respectively. (Extracted with permission from Colodrero et al., 2009 [b])

4. Conclusions

Colloidal chemistry approaches are suitable for implementing optical devices of high quality in DSSC in order to improve their performance. This opens the door for the conscious optimization of the photonic design of DSSC, as is commonly done for their silicon counterparts. This may also open the way to amplifying the absorption of other dyes with low extinction coefficients that cover other regions of the visible and near-IR solar spectrum. In this respect, a thorough analysis in terms of the interplay between the effect of the electrode thickness, the dye absorption spectrum, and the characteristics of the Bragg reflection, such as intensity, spectral position and width, is needed for designing 1DPC based DSSC of optimized performance. On the other hand, the greater enhancement of efficiency attained for thin electrodes coupled to these photonic structures highlight the potential that they might have in other cells using very thin absorbing layers, in which the main source of loss of efficiency is frequently the low amount of light absorbed.

5. References


Photon Management in Dye Sensitized Solar Cells


The present “Solar Energy” science book hopefully opens a series of other first-hand texts in new technologies with practical impact and subsequent interest. They might include the ecological combustion of fossil fuels, space technology in the benefit of local and remote communities, new trends in the development of secure Internet Communications on an interplanetary scale, new breakthroughs in the propulsion technology and others. The editors will be pleased to see that the present book is open to debate and they will wait for the readers’ reaction with great interest. Critics and proposals will be equally welcomed.

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