Full spectrum enhancement of the light harvesting efficiency of dye sensitized solar cells by including colloidal photonic crystal multilayers

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(Received 7 October 2005; accepted 21 March 2006; published online 9 May 2006)

Herein we report a theoretical analysis of the efficiency of dye sensitized solar cells in which colloidal crystals are introduced in different configurations. We find that piling up different lattice constant crystals leads to light harvesting enhancement in the whole dye absorption range. We provide the optimum structural features of such photonic crystal multilayer needed to achieve a photocurrent efficiency enhancement of around 60% with respect to standard dye sensitized solar cells. We demonstrate that this improvement is the result of the optical absorption amplification effect of slow photon resonant modes partially confined within the absorbing part of the cell by the mirror behavior of the colloidal superlattice. © 2006 American Institute of Physics.

DOI: 10.1063/1.2200746

Dye sensitized solar cells (DSSCs) constitute an interesting alternative to solid state semiconductor photovoltaic devices, mainly due to their low cost of production. Briefly, a DSSC is made by a nanocrystalline titanium oxide layer doped with a ruthenium based dye supported on a conducting electrode and fully immersed in a redox electrolyte (typically an iodide solution). The whole system is sealed by a counter-electrode. The dye absorbs light in the visible range and injects the photogenerated electrons to the conduction band of the nanocrystalline titania, being the photoelectrons generated transferred to the supporting conducting substrate. At the other end of the circuit, the electrolyte is reduced at the counter-electrode and oxidized back after transferring an electron to the dye.

Even though current DSSC still shows lower efficiencies than the p-n junction solar cells, there are many parameters to be investigated yet in order to improve light to current conversion. DSSC photocurrent can be increased by using other metal oxides such as NbO₃ or SrTiO₃. Also higher photocurrents can be achieved by changing the sensitized dye, by combining cells with different dyes which absorb at different wavelength ranges or by means of introducing scattering structures that increase the matter-radiation interaction. One step forward in this line were performed adding polydisperse TiO₂ particles at one side of the dye sensitized nc-TiO₂ layer. One step forward in this same direction but applying a different concept was given recently by Nishimura et al., who built the dye sensitized nc-TiO₂ coating within a Grätzel solar cell in the form of a bilayer: One layer with the shape of a highly scattering photonic crystal (PhC) structure, i.e., an inverse TiO₂ opal; the other presents the form of a standard unstructured dyed nanocrystalline titania. This combined structure showed an enhancement of the photogenerated current efficiency of 26% when compared to a standard DSSC. As it has recently been proved, such enhancement comes from the localization of light within the unstructured dyed titania film due to the appearance of photon resonant modes. These resonances occur in systems composed by a photonic crystal possessing an overlayer deposited on top and at spectral regions in which the inverse opal is highly reflecting, i.e., within the photonic crystal pseudogap wavelength range.

Here we demonstrate that a colloidal crystal multilayer, employed as a highly scattering photonic structure combined with an absorbing dye-sensitized nc-TiO₂ layer, leads to a large increase of the photogenerated current for the whole spectrum absorbed by the dye. The light harvesting efficiency (LHE) of a DSSC is defined as:

\[
\text{LHE} = \frac{J}{J_{sc}} = \frac{I_{abs}}{I_{0}}
\]

where \( I \) is the incident photon flux under AM 1.5 spectral irradiance, \( J_{sc} \) is the short circuit current, \( I_{abs} \) is the absorbed current, and \( I_{0} \) is the incident current.

It depends on the extinction coefficient of the dye, its concentration, the thickness of the absorbing layer, and the time of flight of photons within that film. The incident photon to current conversion efficiency (IPCE) is proportional to the LHE and is given by the expression

\[
\text{IPCE} = \frac{\text{LHE}}{\Phi} \frac{q}{F(\lambda)}
\]

where \( \Phi \) is the quantum yield of charge injection, and \( \eta \) is the charge collecting efficiency by the glass supported electrode. From this magnitude its possible to obtain the generated photocurrent density in short-circuit (\( J_{SC} \)) by using the equation

\[
J_{SC} = \int q \text{IPCE}(\lambda) F(\lambda) d\lambda
\]

where \( q \) is the electron charge, and \( F(\lambda) \) is the incident photon flux under AM 1.5 spectral irradiance. It’s clear from Eqs. (2) and (3) that increasing the amount of light absorbed by the dye (or LHE) leads to higher photocurrents. One option to improve the efficiency of a DSSC without substituting any of its components is to structure the materials; it is made of in such a way that the time of flight of photons through the absorbing material is enlarged, thus rising the probability of photogenerating electron-hole pairs. Some attempts in this line were performed adding polydisperse TiO₂ particles at the dye sensitized nc-TiO₂ layer. One step forward in this same direction but applying a different concept was given recently by Nishimura et al., who built the dye sensitized nc-TiO₂ coating within a Grätzel solar cell in the form of a bilayer: One layer with the shape of a highly scattering photonic crystal (PhC) structure, i.e., an inverse TiO₂ opal; the other presents the form of a standard unstructured dyed nanocrystalline titania. This combined structure showed an enhancement of the photogenerated current efficiency of 26% when compared to a standard DSSC. As it has recently been proved, such enhancement comes from the localization of light within the unstructured dyed titania film due to the appearance of photon resonant modes. These resonances occur in systems composed by a photonic crystal possessing an overlayer deposited on top and at spectral regions in which the inverse opal is highly reflecting, i.e., within the photonic crystal pseudogap wavelength range.

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FIG. 1. (Color online) Schemes of the DSSCs whose LHEs are herein analyzed. (a) Standard DSSC made of a nc-TiO₂ film followed by a bulk arranged titania slab of the same average refractive index and length of the compared PhC. (b) A photonic crystal based DSSC in which (b) a single inverse titania photonic crystal with sphere diameter φ₁ (c), two inverse titania PhC multilayer with sphere diameters (φ₂, φ₃), and (d) three inverse titania PhC multilayer with sphere diameters (φ₁, φ₂, and φ₃) of 17 ML each, follow the nc-TiO₂ film.

We seek to find the structural features of the cells depicted in Figs. 1(b)–1(d) that maximize the increment of photocurrent density ΔJ_SC, defined as

$$ \Delta J_{SC} = \int \left[ J_{LEPhC}(\lambda) F(\lambda) d\lambda - \int J_{LEStandard}(\lambda) F(\lambda) d\lambda \right] $$

where LHEPhC is the light harvesting efficiency or absorbance of a dye sensitized solar cell including photonic crystals, and LHEStandard refers to that of the standard DSSC. Both cells compared have the same amount of absorbing material and total width. LHE was calculated in each case using a transfer matrix formalism implementation in a MATLAB code, which allowed us to test a large number of structures in a reasonable time. To simplify, we neglect the vector nature of the radiation and consider just one possible direction of propagation, transforming our problem in a one dimensional (1D) scalar wave one. These assumptions have been repeatedly proven to yield correct results for three dimensional (3D) lattices, as long as only optical effects associated to lower bands are investigated and in a well-defined crystalline direction, as it happens in our case. A detailed discussion on the application of this type of calculations to simulate LHE in solar cells can be found elsewhere.

As starting point, and in order to fix some relevant parameters, we have simulated the spectral response of the LHE of the dye sensitized solar cell described in Ref. 9, with some changes in the order of the components to maximize the efficiency. In Fig. 2(a) the absorbance of both the onephotonic-crystal based DSSC and the standard cell used for comparison are plotted. In this case, ΔJ_SC is maximized when the spherical cavity diameter was φ₁=202 nm. The spectral behavior observed closely fits the experimental observations for the photogenerated current previously reported. With the above mentioned materials characteristics, increments in the photocurrent as large as ΔJ_SC=28% can be achieved, also in good quantitative agreement with the experimental observations presented in Ref. 9. The effect
plotted a two-dimensional lattice constants of the photonic crystal multilayer, we have
of stacking a second and a third inverse titania opal with a different lattice parameters after the dye sensitized titania layer, as in Figs. 1(c) and 1(d), is to extend the wavelength range at which optical absorptance enhancement occurs, as can be clearly seen in Figs. 2(b) and 2(c). Widening the LHE amplification range yields a largely improved performance of the DSSC, a photocurrent increment of $\Delta J_{SC}=48\%$ being estimated for the optimized structure in the case of two inverse opals (spherical cavities with diameters $\phi_1=234$ nm, $\phi_2=204$ nm, and $\phi_3=178$ nm). With this latter structure it is possible to attain a colloidal crystal mirror able to provide LHE enhancement over most of the absorption range of the ruthenium dye. This structure is feasible and provides an extraordinary increase with respect to previously proposed ones. We have also carried out calculations including a larger number of photonic crystals in the DSSC. Only a slightly larger enhancement is achieved with respect to the three-opal stacking. Since almost all the absorption spectrum of the dye is already amplified with three crystals, hence the improvement would not justify the effort of building a more complex structure.

In order to visualize the dependence of $\Delta J_{SC}$ with the lattice constants of the photonic crystal multilayer, we have plotted a two dimensional (2D) contour plot of $\Delta J_{SC}$, keeping constant the diameter of the cavities in the bottom opal at its best value, $\phi_3=178$ nm, and varying $\phi_1$ and $\phi_2$. This photocurrent enhancement map is shown in Fig. 3. The abscissas correspond to the sphere diameter of the middle crystal ($\phi_2$) and the ordinates to that of the cavities of the top crystal ($\phi_1$), the one in contact with the absorbing layer. We can see that this map is almost symmetrical with respect to the $\phi_1=\phi_2$ line, indicating that, once a triplet of optimum diameters is found, the order in which the colloidal crystals are arranged does not substantially modify $\Delta J_{SC}$. The inner shell diameters that maximize the photocurrent enhancement (up to 61%) are $\phi_1=234$ nm, $\phi_2=204$ nm, fixed $\phi_3=178$ nm. The enhancement rapidly decreases as one of the diameters gets too large or too small so the corresponding photonic crystal effect does not match the absorption range of the ruthenium dye any longer.

Enhancement of LHE takes place at wavelengths corresponding to the stop band of the photonic crystals involved. Such enhancement occurs at resonant modes which are partially localized within the absorbing dyed layer as a result of the mirrorlike behavior of the opals deposited behind it, as it has recently been shown by some of us.$^{10}$ Partially confined photons travel slower through the absorbing layer and are more likely to be absorbed. Interestingly, the photonic crystals do not need to absorb, as it was originally assumed.$^{9}$ If the presence of the anchored dye is also considered in the titania colloidal crystals, the simulated LHE increment would lead to lower $\Delta J_{SC}$ than for the cases discussed above. It must be noticed that the absolute values of the photocurrent density enhancement are not necessarily lower in cells in which dyed opals are introduced, since the amount of the absorbing dye is also much larger. What our calculations prove is that a more efficient use of the material is done by placing nonabsorbing photonic crystals, since most of the light is harvested within the unstructured, dye sensitized nc-TiO$_2$ coating onto which the colloidal lattices are deposited.

To conclude, we have made a theoretical analysis of the performance of a dye sensitized solar cell in which inverse titaniaopal multilayers are included. We have found the optimum structural features to build the most efficient solar cells based on this approach. We foresee that this substantial improvement might not only lead to more competitive dye sensitized solar-to-electric energy conversion devices, but also find applications in related fields such as photocatalysis.