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ABSTRACT

Self-assembled synthetic opals are suitable for integration into solution-processed thin film solar cells. In this work, finite-difference time-domain simulations are carried out to tailor optical properties of monolayer and multilayers of semiconductor spheres to trap light when these structures are incorporated into thin film solar cells. In particular, architectures in which spheres are filled with a photoactive material and embedded in a lower refractive index medium are examined. Based on spectra and field intensity maps, this study demonstrates that opal-like photonic crystals obtained from colloidal templates and filled with light-absorbing material can significantly harvest light by exploiting photonic band resonances.

Keywords: Opal structure, Light-harvesting, perovskite

1. INTRODUCTION

Many efforts are devoted to PV technologies due to their significant participation in the energy challenge. A large number of PV concept and technologies are studied with the aim to find efficient and low cost solutions to this energy challenge. As example Dye-Sensitized Solar Cells (DSSC) are fabricated by soft processes which results in a fabrication cost five times lower than conventional Si cells. « Classical » DSSC’s are composed of a porous semiconductor (TiO2) of several microns, sensitized by a dye. A liquid electrolyte, allowing charge transfer and regeneration of the dye, is sandwiched between the photoanode and a counter-electrode.

The presence of the liquid electrolyte impedes the commercialization of such PV modules. Efforts are then devoted to the fabrication of all-solid DSSC’s. However, solid electrolytes [1] result in lower efficiencies, due to a low charge mobility and incomplete pore filling of the photoanode [2]. All-solid solar cells therefore need innovating solutions: new dyes, decrease of the thickness [3] and control of the porosity[4].

1.1 Perovskite solar Cell

Recently, new perovskite compounds have allowed preparing highly efficient solid-state solar cells [5 - 7] (15%). Those compounds can be used either as inorganic sensitizers deposited on porous semiconductor, or as light absorber and electron transporting material in the same time. In both approaches, the thickness is reduced to less than 1 micron, taking into account the balance between the maximal light absorption and charge transfer inside the materials. In order to increase the efficiency, it is proposed in this paper to optimize further light collection and monitor charge transfer at the interfaces, thanks to the design of new materials with controlled architecture [8]. We have implemented templating techniques to prepare perovskite photoanodes with an inverse opal structure [9-10]. This photonic structure will increase light collection, light scattering and reduce reflexion losses, as well as favor organic electrolyte infiltration. The interpenetration of electrolyte and photoanode will enhance charge separation at the interface. The recent discovery of organo-metal halide perovskite materials to replace the dye in DSSC’s gave them a renaissance. Although the organometal halide perovskites have been widely studied for decades, they were first envisaged as photo- or ionic conductors and semiconductors for organic light-emitting devices and thin film transistors.

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The electronic and dielectric properties of these perovskites strongly depend on their stoichiometry and crystal structure details. They have received increasing attention as solar cells constituents due to their panchromatic absorption, ambipolar charge-carrier mobilities, high absorption coefficient, long exciton lifetimes/diffusion length.

CH3NH3PbX3 (X=I, Br) was firstly used in 2009 and 2011 as visible-light sensitizer, in the form of quantum dots deposited on the mesoporous TiO2 photoanode in a classical DSSC containing liquid electrolyte. The conversion efficiencies were first moderate but interesting (η = 3.13 to 3.81%). Later in 2011, Park et al. raised the efficiency up to 6.54% by changing the solvent and tuning the titania surface[11]. However, the perovskite particles were not stable against liquid electrolyte. This issue was addressed in 2012 when a photon-to-current efficiency of 9.7% was obtained by Graetzl and Park, using the tri-iodide perovskite as sensitizer onto mesoporous TiO2, in combination with the widely-used Spiro-MeOTAD (2,2',7,7'-tetrakis-(N,N-dimethoxyphenyl-amine)-9,9'-spirobifluorene) solid hole transporting material. Soon after, Snaith and Miyasaka discovered that the semiconductor titania semiconducting scaffold could be replaced by an insulating material such as Al2O3, in combination with mixed iodide-chloride perovskite, therefore proving that the perovskite layer could act both as the light harvester and the electron transporting material (n-type semiconductor).

Since 2013, different deposition techniques and fabrication engineering have allowed to reach efficiencies over 15%: either from solution (one-step or sequential deposition) or by evaporation (dual-source vapor deposition and vapor-assisted solution process).

As it can be noticed, the power conversion efficiency of perovskite-based solar cells has increased 5 times from their first reported value in 2009 to the present day, now exceeding 18%, making them competitive with thin films PV technologies. Accordingly, perovskite solar cells have quickly become a hot topic, what can be confirmed by the growing number of papers devoted to their preparation and characterization.

1.2 Opal structure

Photonics crystals have properties that are not found in bulky classical material. The structuration of materials with periodic or quasi-periodic architecture defines new properties of light interaction. Photonic crystals, which are artificial materials with rationally designed properties, can allow both field components of light to be coupled to meta-atoms, enabling entirely new optical properties. The modulation of refractive index is one of the most fundamental characteristics of light propagation in materials in photonic crystals. During the last twenty years, many efforts were devoted to the study of optical properties of dielectric structures exhibiting a periodic distribution of their refractive index. Their optical properties - and, in particular, their reflectance or absorbance properties – are strongly dependent on the Bragg diffraction which takes place in such a periodic medium and spectrally defines the reflected or absorbed light range reflected or absorbed. The simple linear frequency-wavenumber relation found in a homogeneous material is thereby replaced by a more complex photonic band structure and, when the circumstances (symmetry, contrasts of indices,) are favorable, “photonic band gaps”, i.e. continuous ranges of frequencies where propagation is forbidden in any direction and for any polarization, can appear and then enhance the absorption properties which is one objective of this project. Even if there are many unusual optical properties associated with these gaps, they turn the material into a perfect reflector or absorber for a range of frequencies what is really useful for photovoltaic applications. This can be seen as a further advantage: by changing the geometry of the photonic crystal, the selectivity of the surface reflectance can be strongly modified, leading to spectacular absorbance and iridescence effects.

Human efforts have recently been devoted to the development of artificial structures showing these properties. The tremendous effort is driven by the hope to develop new optical devices useful for application in photovoltaic systems.

2. NUMERICAL METHOD

The method chosen to design innovative perovskite solar cells is Finite-Difference Time-Domain (FDTD) method. FDTD simulations were performed using Meep [12], a freely available software package. Finite-Difference Time-Domain (FDTD) [12] is a full-vectorial numerical method of solving Maxwell’s equations relying on discretization of both space and time, which was first introduced by Yee [13]. In this algorithm, physical space is represented as a space...
lattice made of cubic unit cells with edges of length $\delta l$. Each cell contains all the electromagnetic field components in such a way that the divergence equations are satisfied. These fields are then propagated in both space and time according to curl equations. In order to achieve this, physical time is divided into consecutive time steps $\delta t$. FDTD is a method of choice to analyze light propagation in a structure that has a size comparable to light wavelength or lower. This general, simple and straightforward method allows computing directly the response of a photonic structure to a short Gaussian pulse corresponding to a broad range of frequencies.

### 2.1 Simulation domain

Figure 1 depicts the rectangular cuboid computational domain used to carry out simulations. This domain was delimited by so-called adiabatic absorbers [14], and Bloch-periodic boundary conditions. A unit cell of the periodic structure is also represented at the center of the computational domain. In this case, this is a monolayer of dielectric spheres photonic crystal. A time-dependent current planar source (S) was used to generate an electromagnetic polarized plane-wave pulse in the incident medium. Transmission and reflection spectra were computed at the detection planes (T and R) in a two-step process. Firstly, a simulation was carried out in an empty computational domain to detect incident field at each time step and to accumulate its Fourier transform. Secondly, frequency-dependent transmitted and reflected fields on the optical structure were computed. These data allowed to assess power spectra and to normalize them to finally obtain reflectance and transmittance.

![Simulation domain](image)

**Figure 1**: left: FDTD simulation domain. At the two extremities along $z$, the simulation domain ends with adiabatic absorber layers. Periodic boundary conditions are applied at the four vertical faces. A monolayer of spheres lies at the center of the domain. Transmission (T), reflection (R), and source (S) planes are also represented. right: Normalized intensity $I/I_0$ of a Gaussian source traveling in free space, as a function of frequency $\nu$ (in normalized units) and as a function of wavelength $\lambda$. $\nu_0 = 2.02$ and $d\nu = 0.93$.

Perfectly matched layers (PML) are layers that are placed at the extremities of the simulation domain in order to truncate it. They are purely mathematical constructions built to gradually absorb light penetrating them. Their role is to prevent light from being reflected on the simulation domain boundaries.

A continuous source produces waves at only one frequency. It is trivial to check if it works well. A Gaussian wave is characterized by its center frequency $\nu_0$, its full width at half maximum (FWHM) $d\nu$, and its maximum height $I_0$. The exact value of this last quantity does not really matter for simulation whose purpose is to compute normalized spectra. Figure 1(right) depicts the normalized intensity corresponding to a Gaussian pulse emitted in empty space.
2.2 Dielectric function reduction

In this type of work, material optical properties have to be carefully taken into account in order to reach the desired accuracy. We’ve defined two models. In model 1, polarization instantaneously responds to electric field excitation in matter. Therefore, the dielectric constant is real and does not depend on frequency [6]. Hence, there is neither dispersion, nor absorption in such a perfect material. On the other hand, in model 2, matter is not considered to be perfect and electric susceptibility does depend on time. Therefore, material dispersion and absorption are integrated into the model. Material dispersion was taken into account through the use of Lorentz dispersion laws (reduced dispersion models) for dielectric and semiconductor materials.

These two models are complementary since structures made of perfect materials shows optical responses that only depend on geometry, while structures with optical properties taking dispersion and absorption into account display much more complex and intricate behaviors depending on the frequency of light.

Material optical properties appear in Maxwell’s equations through the complex relative dielectric function $\varepsilon = \varepsilon' + j\varepsilon''$. Both real and imaginary parts of the dielectric function are directly connected to material refractive index $n$ and extinction coefficient $\kappa$, which determine light propagation and absorption inside media. Material optical dispersion, i.e. the dependency of $\varepsilon$ upon electromagnetic wave frequency, can be integrated into FDTD simulations. Experimental data of $\varepsilon(\omega)$ in tabulated form cannot be directly encoded into a FDTD program because the algorithm deals with fields in the time-domain and not in the frequency domain. Therefore, a dispersion law reproducing $\varepsilon_{exp}(\omega)$ has to be delivered to the FDTD program as input to account for material optical properties. The parameters of these models are obtained by fitting the experimental data $\varepsilon_{exp}(\omega)$, and are then directly used in the time-stepping equations.

3. OPAL STRUCTURE

As a reminder, the aim this paper is to present new architectures based on opal structure to improve light and charge collection. Figure 2 depicts architecture studied in this paper. The main feature of these cells is to incorporate a photonic crystal (opal or inverse opal) to manipulate light and increase its collection in the solar cell through light trapping strategies. This architecture should also allow good material infiltration and good charge separation at interfaces due to the increased contact surfaces. Multiple structures have been studied, from single layer to trilayer. The last one can be derived in FCC and HCP arrangement.
In order to compare all these structures in the way they can harvest light, we must consider the solar spectral irradiance $I_\lambda$ at AM 1.5. This spectrum results from the black body emission of the sun, the absorption and scattering of incident light by the atmosphere, and carries the blueprint of the terrestrial atmosphere chemical composition.

A more relevant quantity to consider is the spectra photon flux $\phi_\lambda = \frac{I_\lambda \lambda}{hc}$, which represents the flux of photon reaching the solar cell per unit wavelength. For our purpose, we can make the hypothesis that each photon absorbed inside the solar cell leads to the creation of an e-h pair. As depicted in Figure 3, we see that the photon flux increases with $\lambda$, meaning that light-harvesting at the red edge of the visible spectrum should be particularly emphasized.

From the absorbance spectra $A_{\text{photonic}}(\lambda)$ and spectral photon flux $\phi_\lambda$, one deduces the e-h generation rate:

$$G_{\text{photonic}} = \int_{\lambda_{\text{min}}}^{\lambda_{\text{max}}} A_{\text{photonic}}(\lambda) \phi_\lambda d\lambda.$$

One can then compute the e-h generation rate gain $\Delta G = G_{\text{photonic}} - G_{\text{film}}$ that the photonic structure brings compared to a simple thin film solar cell including a layer of perovskite with an equivalent thickness so that there is the same perovskite quantity per unit area in both solar cell. Normalized variation shows that $\Delta G$ increases linearly up to $D = 350 \text{ nm}$ for each structure. After that threshold, it is more or less saturates for the monolayer structure, while it decreases for $D > 400 \text{ nm}$ for higher number of layers. This graph means that one can obtain the best enhancement with monolayer structures. Therefore, for a given quantity of perovskite, one should make a monolayer of dielectric sphere out of it to maximize light-harvesting.
Figure 3: Solar spectral photon flux $\phi_\lambda$ AM 1.5 as a function of wavelength $\lambda$.

Figure 4: Integration over the full solar cell spectrum of light collected by the opal structure. The normalized enhancement compared to the equivalent film thickness ($\frac{\Delta G}{G_{film}}$) is presented as a function of sphere diameter $D$ for different multilayer structures.

5. CONCLUSIONS

In this paper we presented the preliminary results of templating perovskite solar-cell with an opal-like structure. FDTD numerical tool has been used under Meep formalism to assess the performances of such structure. It has been shown that perovskite opal structure creates an enhancement of the light harvesting. These results open a new window on solutions to improve perovskite solar cell efficiencies.
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7. REFERENCES