Modeling and fabrication of luminescent solar concentrators towards photovoltaic devices

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Abstract

Sun light concentration is a way to decrease photovoltaic devices cost. An original method to concentrate light is the use of Luminescent Solar Concentrators (LSC), which act as waveguide to concentrate light towards the photovoltaic (PV) cells. To improve the LSC efficiency, the addition of a Photonic Band Stop (PBS) is investigated. Simulations were realized for different systems, with and without PBS. They enabled to distinguish loss mechanisms, and to determine what improvement may be expected with an additional photonic component. Then LSC and PBS were realized and characterized. The fabrication of the complete device coupling the both parts is challenging.

Keywords: luminescent solar concentrator; photovoltaics; photonic crystal; nanoparticles

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1. Introduction

Light concentration photovoltaic systems have been developed in the past decades following the trend that light management is becoming a key issue in the improvement of photovoltaic (PV) solar cells. The aim of concentration is to achieve cost reduction through semiconductor material saving and efficiency enhancement due to high light injection level. Most concentrating systems use lenses and mirrors to concentrate the direct sunlight hundreds of times (typically x400-x700) on solar cells [1,2]. Nevertheless, high concentration photovoltaics (HCPV) needs sun-tracking systems and the diffused sunlight is lost. Due to these constraints, concentrating systems are only suitable for sunny regions with efficient solar cells and for structures without weight limits. On the contrary, low concentration photovoltaics (LCPV), which has also been developed, is cheaper and may concentrate both direct and diffuse sunlight. Being mainly non imaging, LCPV has consequently a different scope of application than high concentration PV systems.

Luminescent Solar Concentrator (LSC) is a popular example of low concentration photovoltaics, studied since the early 1980s [3] and being now subject of numerous researches [4,5]. The principle of LSC is to trap light inside a dielectric matrix doped with organic or inorganic dyes until it reaches the cells. A part of the sunlight is absorbed by the dye particles and isotropically emitted, allowing a portion of light to be trapped by total internal reflection.

Theoretically, this concept is appealing because concentration factors up to 1000 without tracking are possible [6]. Practically, experimental performances fall far from this expectation. Sloof et al. obtained the world record of solar-to-electric conversion efficiency per unit collector surface of 7.1% [7] and many other research teams reached efficiency around 3% to 6.7% [9,10]. However, the common point of record LSC systems is their small sizes, which indicate that losses are highly dependent of the optical path.

To improve the concentration factor, a Photonic Band Stop (PBS) may be added or integrated to the luminescent layer, in order to mainly avoid front surface losses [11]. Indeed without PBS some photons may escape from the doped matrix. With PBS, these photons are reflected back into the LSC and then are more able to reach one of the solar cells. In this work, the different sorts of losses and the concentration factor were simulated, with and without PBS, in order to evaluate the potential enhancement of concentration factor and efficiency.

In parallel, LSC and photonic crystal were synthesized and characterized. The assembly of the both parts is finally investigated.

2. Luminescent Solar Concentrator description

The studied device is based on a rectangular LSC. PV cells pave the reflective back surface with a coverage fraction \( f \) which may be variable. The concentrator matrix is often composed of a dye doped polymer layer. This configuration is named “bottom-mounted” opposite to configurations in which PV cells are on the left and right sides of the concentrator matrix. These both configurations are equivalent in term of potential conversion efficiency. Figure 1a shows a scheme of this type of LSC with all losses which may occur in such a system.
In this work, the polymer used is polymethylmethacrylate (PMMA) and the doping dye is a commercial dye from BASF named Lumogen RED305® (R305). Its absorption and emission maxima are centered on 578 nm and 613 nm respectively (Fig. 1b). With our Perkin-Elmer spectrophotometer (Lambda 900), similar spectra were obtained.

With PBS, the structure will have the same geometry, the PBS being deposited on the front surface of the LSC matrix.

3. Modeling and fabrication of LSC

These simulations are realized with a home-made Ray-trace Monte-Carlo code.

3.1. Simulations of losses and Photonic Band Stop interest

Simulations are realized on a LSC system, with and without PBS at the front surface, with $10^5$ photons tested in parallel. The selected PBS is an opal filter which reflects or transmits photons, according to the bandgap and the reflection spectrum. PBS optical properties are angular dependent but in a first approach, only the normal incidence was considered. Some LSC parameters are considered ideal. Therefore the dye quantum yield is set to 100 % (real value varies between 95% and 99%, depending on the solvent) and the back reflector has also a perfect reflection coefficient whatever the wavelength is. The matrix is considered as perfectly transparent and the cell coverage fraction $f$ is of 1/100. We also choose periodic boundary conditions. The dye has been modeled using R305 absorption and emission coefficients measured on Perkin-Elmer Lambda 900 spectrophotometer.

In figure 2, losses and absorption of photons by the cells are represented. Without PBS (Fig. 2a) only 16.1 % of the light is converted (blue line). External losses represent the fraction of photons that do not enter the system and losses due to mirrors (black line). Escape losses are defined as the fraction of photons which is re-emitted by the dye and which escapes the device by the front surface (red line). Without PBS, these losses are very significant and amounted to 79.9% of the photons re-issued. The absorption line (purple line) follows the Beer Lambert law, with $c$ the light speed, $\alpha$ the absorption coefficient of the matrix, and $d$ the LSC thickness. In this configuration, we consider a return trip, therefore the $2d$ term.
Figure 2b shows simulations of losses and absorption of the cell covered with a PBS. The front losses have drastically decreased (4.5%) and the light converted by the cell is of 40.1%. But the fraction of photons not captured by the system increases in the same way: 55.4% vs. 4% without PBS.

Otherwise, concentration factor vs. coverage fraction for an ideal system with and without PBS are simulated (Fig. 3). The coverage fraction may be defined in this work as the total PV cell area divided by the total area. It is evident that the concentration factor is improved with the presence of a PBS.

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![Figure 2](image1.png)

**Fig. 2.** Simulations of losses and of the cell absorption without (a) and with (b) PBS.

![Figure 3](image2.png)

**Fig. 3.** Concentration factor vs. coverage fraction for an ideal system with (red stars) and without (black circles) PBS.
Simulations developed in this part show that a PBS at the LSC front surface allows to reduce losses, particularly front losses and to increase the concentration factor. But the main disadvantage of this added layer is the decrease of the fraction of captured photons. A trade-off must be found and the spectral mismatch reduced.

3.2. LSC fabrication

The LSC matrix is composed of methylmethacrylate (MMA) and polymethylmethacrylate (PMMA). Dye is added in the solution and then azobisisobutyronitrile (AIBN) is used as initiator for the polymerization. The matrix choice was driven by the characteristics required for photovoltaic applications, particularly its transparency, its refractive index ($n_{PMMA} = 1.49$) and the capability to efficiently dissolve a dye. This mixture is then poured in a glass and silicone mold. The polymerization takes place in a water bath at constant temperature, typically between 60°C and 80°C [12].

4. Photonic Band Stop (PBS): synthesis and characterization

4.1. PBS choice: opal structure

In a first approach and to demonstrate the feasibility concept, the opal silica structure was chosen. Actually, it is a well-known structure, easy to synthetize. Composed of silica nanoparticles, it is a low-cost material, eco-friendly. Moreover, the bandgap is adjustable to the required wavelength and its optical properties are well adapted to the envisaged device.

The challenging points are to obtain monodisperse particles with the expected diameter, to realize a homogeneous deposition on PMMA with the optical properties required.

4.2. Experimentals

Silica nanoparticles syntheses are based on the Stöber method [13,14,15] which uses the hydrolysis and condensation of tetraethyl orthosilicate (TEOS). The starting solutions were TEOS (99,999%, Aldrich), absolute ethanol (99.8%, VWR), ammonia solution (32%, Merck), and deionised water. The reactants were used as purchased without further purification.

The nanoparticles diameter is determined by the well-known equations [14]:

$$\lambda_{111} = \frac{2}{\sqrt{3}} d \times \sqrt{n_{air}^2 - \sin^2(\theta)}$$  \hspace{1cm} (1)

$$n_{eff} = \sqrt{n_{air}^2 (1 - f_{sphere}) + n_{SiO2}^2 \cdot f_{sphere}}$$  \hspace{1cm} (2)

with $\lambda_{111}$ the characteristic wavelength corresponding to a Bragg reflection from the {111} planes, $d$ the sphere diameter (nm), $n_{air}$ the air refractive index, $n_{SiO2}$ the PBS refractive index ($n_{SiO2} = 1.44$), $f_{sphere}$ the volume fraction ($f_{sphere} = 0.74$ in our cfc structure), and $\theta$ the light incidence angle. In our case with R305 dye, the opal must reflect light of the emission spectrum, consequently the corresponding diameter is of 280 nm.

Two solutions are needed: one containing ammonia (4.15 mL) and deionised water (0.85 mL), the other containing TEOS (0.5 mL) and ethanol (55 mL). The second solution is quickly added to the first under rapid stirring at 30°C (solution A). After about 3h, nanoparticles may be physically separated from the liquid phase and redispersed into deionised water or absolute ethanol.

The seeded-growth technique was also experimented, and in this case, after 3h, a solution B containing TEOS (1.132 mL) and ethanol (10 mL) is added drop by drop into the solution A, still under stirring and at 30°C. After about 2h under these reaction conditions, particles may be considered having their final size. This last step improves the monodispersity and the spherical shape of the particles, which is confirmed by SEM images (FEG-SEM Zeiss...
Merlin VP): under these conditions, spherical silica nanoparticles were obtained with an average diameter estimated at 280 nm (Fig. 4a).

![SEM image of home-made nanoparticles with an average diameter of 280 nm](image1)

![Nanoparticles deposited by spin-coating on glass substrates](image2)

Fig. 4. (a) SEM image of home-made nanoparticles with an average diameter of 280 nm; (b) Nanoparticles deposited by spin-coating on glass substrates.

Opals are then produced by spin-coating deposition at room temperature (table-top SPIN150™-NNP processor). The spin-coating process involves centrifugal forces for spreading the solution initially deposited at the center of a flat substrate. In this process, the main parameters to control the quality and final thickness of the photonic structure are speed, viscosity, acceleration and duration. After a lot of parameters combinations, it seems that nanoparticles dispersed in absolute ethanol and deposited at 150 rpm and 100 rpm/s during 15 min allow obtaining a promising opal structure, as shown in figure 4b.

Natural sedimentation was also experimented as an alternative solution to synthesize PBS. But, this process was too long (minimum 5 days) and was not pursued.

For the test samples, glass substrates are used, because of its good wettability properties and cleaning ease.

4.3. Optical characterizations

The UV-Vis transmittance spectrum at normal incidence of the opals shows that a photonic band-gap effect is observed around 620 nm, which results from Bragg diffraction due to the periodicity in the location of the nanoparticles (Fig. 5a). Three home-made samples were measured: two spin-coated samples (5 μm and 20 μm thick respectively), and one deposited by natural sedimentation with a thickness of 20 μm. As expected, the fraction of transmitted light is more important in the case of the thinner layer. Nevertheless, the photonic bandgap is located at the same wavelength of about 620 nm for each sample. This optical property is a good proof of the quality of the deposition and of the nanoparticles monodispersity [16].
Fig. 5. (a) Transmission spectra of three different home-made samples: spin-coated samples with two different thicknesses (5 μm (red line) and 20 μm (black line)) and one by natural sedimentation (20 μm thick, blue line). (b) Reflexion spectra recorded at different angles of incidence from a home-made spin-coated sample. The spectra show that the position of $\lambda_{\text{max}}$ shifts to shorter wavelength as the angle of incidence increases: it is an evidence of a pseudo band stop existence.

Fig. 5b shows UV-Vis reflectance spectra which are measured at different incident angles from 0° to 70° on a home-made spin-coated sample. The reflectance maxima shift to shorter wavelengths what is in accordance with the literature [17]. This sample does not present a complete photonic bandgap, since incident wavelengths forbidden at normal incidence can be transmitted more easily through the crystal at other angles. It has been also verified that no absorption occurred in our films, only reflection and transmission.

4.4. Deposition of PBS on LSC

In a same way as on glass substrates, opals were deposited by spin-coating on LSC. Due to PMMA wettability, the nanoparticles organization is not as efficient as on glass. The deposition parameters must be adapted: with 500 rpm and 500 rpm/s, during 30 seconds, photonic effect was observed but only on small surfaces. This process is still examined and will allow the efficiency measurement.

5. Conclusion

This work may be divided into two main parts: on one hand the modeling of LSC with and without PBS deposited on the front surface, and on the other LSC and silica nanoparticles syntheses followed by opal structure deposition.

Simulations have shown that to combine PBS with LSC allows enhancing the converted light but the decrease of the front losses is weight against by the increase of the fraction of non-captured photons.

Using a seeded-growth technique, monodisperse and spherical silica nanoparticles were obtained with a diameter in accordance with the dye spectra. Deposition and opals formation were realized and optimized by spin-coating. Their optical properties were measured, a photonic bandgap is observed and the angular behavior is in accordance with the literature.

Then the coupling between PBS and LSC was realized by spin-coating too, but wettability and adherence must be optimized.

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References


