Apollony photonic sponge based photoelectrochemical solar cells†

Fernando Ramiro-Manzano,[a] Pedro Atienzar,[b] Isabelle Rodriguez,[a] Francisco Meseguer,*[a]
Hermenegildo Garcia[b] and Avelino Corma*[b]

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We have developed a quasi-fractal colloidal crystal to localize efficiently photons in a very broad optical spectral range; it has been applied to prepare dye sensitized photoelectrochemical solar (PES) cells able to harvest very efficiently photons from the ultraviolet (UV) and the visible (VIS) regions of the solar spectrum.

Since the discovery of dye-sensitized photoelectrochemical solar (PES) cells by Gratzel[1] in the nineties, attempts to solve the general problem of an efficient harvesting of sunlight have mostly arisen from the chemistry and photochemistry side. In contrast, the optimization of solar cells based on light scattering phenomena, is still missing. In order to increase light harvesting, some groups have either deposited scattering layers of large titania particles,[2] or they have inserted spherical voids (around 200–300 nm) in the electrode.[3] In all cases, the scattering centers produce modest enhancement in the PES cell efficiency. The use of Photonic Crystal (PC)[4] based solar cells[5] is very attractive, as photons near photonic band gap edges can be slowed down at the active material to increase the photocarrier generation efficiency. However, light localization effects in a PC photovoltaic cell are restricted to small frequency regions of the solar spectrum. It would be desirable to find new photonic architectures able to localize photons of the whole solar spectrum near the photoactive medium. In this way, the knowledge of strongly scattering systems[6] can help to design new solar cells able to harvest light in broad spectral regions. Most of the work published so far, concerns materials formed by isolated or interconnected high refractive index particles (titania,[7] GaAs,[8] GaP,[9] Ge,[10] *etc.*) with a porosity value below 60%. TiO_2 is a very appropriate scattering material, as it is transparent to visible light and possesses a high refractive index value ($n = 2.7$).[11]

In this Communication we present a new solar cell architecture, based on the Photonic Sponge (PhS) concept.[12] It is formed from a quasi-fractal distribution of interconnected spherical cavities in the active medium.[13] The PhS we describe here is based on colloidal crystals with quasi-Apollony[14] fractal ordering. Also, the cavities have very different sizes, able to strongly scatter photons from the UV and VIS regions. Fig. 1 shows a scheme of a two-dimensional (2D) projection of the Apollony packing. It is expected it can induce strong light localization effects as has recently shown for similar fractal structures.[15] In our case we have built up the inverted topology using the templating method like that employed to fabricate titania[16] inverse opals. For such a purpose, a quasi-fractal colloidal template was grown. An aqueous suspension of latex spheres (IkerlatPolymers) of 1500, 400, 300 and 150 nm with a proportion of 82 : 12 : 4 : 2, respectively, to favor Apollony packing, has been used. TiO_2 particles were synthesized within the interparticle pores of the thin porous film by decomposition of titanium isopropoxide (see ESI†). Then, the latex template was selectively removed at 450 °C to obtain the inverse structure. The thermal process induces the transformation of the TiO_2 into anatase, and also improves the electrical connectivity between nanoparticles. For the sake of comparison, we have also made twin reference samples of titania nanoparticles paste produced with the same physico-chemical method but lacking the PhS architecture. Both PhS and reference samples have the same thickness value (23 μm).

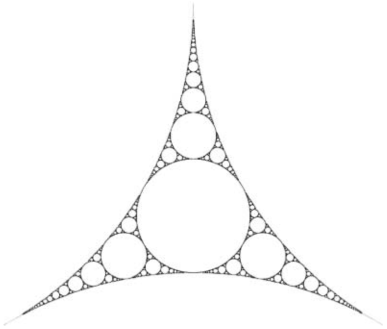

Fig. 1 Scheme of the 2D projection of an Apollony fractal distribution.

Fig. 2a shows the SEM images of the PhS. It can be seen that our PhS structure presents a random distribution of spherical air cavities (from 0.1 to 1.5 μm) surrounded by a high refractive medium formed by connected TiO_2 nanoparticles. The pores are interconnected with each other resulting in a macroporous membrane with a high porosity value of 85%. Also, in some regions (see inset in Fig. 2a), one can see the tendency to fractal ordering, with smaller pores located at the intersection of three neighbor large cavities, being quite similar to the scheme shown in Fig. 1. Here, at variance to previous PhS's published so far, samples are formed from interconnected voids (instead of connected particles) in where enormous light scattering effects are expected. This can be compared to the SEM image of the reference sample (Fig. 2b). At variance to the PhS topology, it shows a plain thin film composed of titania nanoparticles with a much smaller porosity value (23%).

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[a] *Centro Tecnologico de Ondas. Unidad Asociada ICMM-CSIC/UPV. Universidad Politecnica de Valencia, Av. Los Naranjos s/n, E-46022, Valencia, Spain. E-mail: fmese@fis.upv.es; Fax: +34 963879849; Tel: +34 963879841*
[b] *Instituto de Tecnologia Quimica. CSIC-UPV, Universidad Politecnica de Valencia, Av. Los Naranjos s/n, E-46022, Valencia, Spain. E-mail: acorma@itq.upv.es; Fax: +34 963877809; Tel: +34 963877800*
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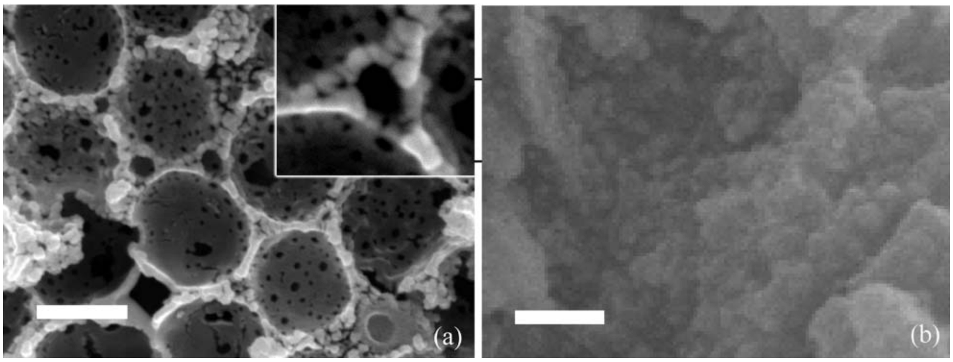

Fig. 2 SEM images of titania nanoparticles arranged in a PhS architecture (a) or in a packed manner (b). One can see in (a) how the smaller cavities arrange in the regions between the larger ones. Scale bars: 1 μm.

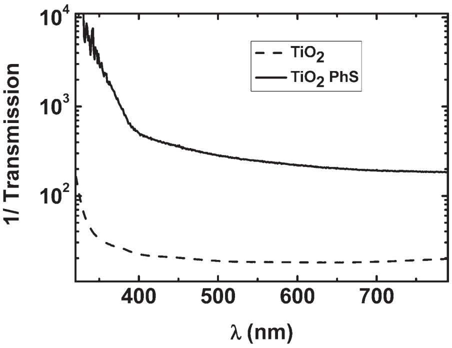

Fig. 3 Inverse of transmittance *versus* wavelength for TiO_2 thin film made of nanoparticles with a topology of PhS (continuous line) and a plain film (dashed line).

Optical transmission experiments of PhS samples, in the whole UV, VIS and near infrared (NIR) spectra (not shown here), show a much larger scattering efficiency as compared to the reference ones. We will concentrate on the spectral region (320 nm to 800 nm) covered by the PES cells.[1] Fig. 3 shows the inverse of transmission of both the PhS and the reference samples (see ESI†). The only difference between them is the much higher porosity of the PhS sample. Several consequences can be extracted from the data. Firstly, at wavelength values far from the absorption edge of titania (380 nm), PhS samples show a transmittance value one order of magnitude smaller than that of plain titania thin films. Also, as the porosity value of the PhS structure is very large, the mean value of the refractive index, $\langle n \rangle$, is very low (around $\langle n \rangle$ = 1.30). Therefore, photons are hardly reflected at the air–PhS interface (see ESI†). Secondly, the scattering effects appear not in a narrow spectral zone (as happens for the PC case) but it covers the whole visible region useful for PES cells. In this region, bulk titania presents a negligible optical absorption. Therefore, one can conclude that visible light is scattered ten times more efficiently by titania nanoparticles, when PhS architecture is used. As the porosity value in the PhS is 3.7 times larger than that of the reference sample, the scattering cross section density (defined as the scattering value per gram of the scatterer material) is enhanced about 40 times when PhS architecture is used. Finally, the transmittance ratio between the PhS topology and the standard system is dramatically enhanced near the fundamental absorption edge of titania, being about 50 times stronger at 380 nm. In this region, near the absorption edge, the refractive index contrast titania/air increases enormously. Therefore, light scattering effects are enhanced as it was predicted by Genack[11] and later showed for GaP networks.[9] Therefore, the scattering cross section density, in this spectral region, is about 180 times larger than that for the standard titania film.

As a matter of fact, PhS systems present the ideal architecture to harvest photons from the whole solar spectrum. PhS plays the role of a quasi-perfect light trap, *i.e.* most of the incident photons enter inside the system and, then, they are trapped in the high refractive index network. This new topology can be of application for photovoltaic generation in titania based dye sensitized PES cells. From a naïve argument, photocarrier generation should be proportional to the absorption coefficient of the active material (either titania nanoparticles or the photosensitized dye) times the photon is scattered at nanoparticles. Therefore, one should expect that electron photogeneration in PES devices can be much more efficient when the active material has a PhS topology.

In view of the above results and their potential application to an efficient light harvesting for photovoltaics, a photoelectrochemical solar cell with a PhS topology has been constructed (see ESI†). For comparison purposes, standard PES cells were built with the same thickness and chemical method as for the PhS one. It is important to stress the much higher porosity of the inverse opal topology (with a 85% of void volume). Therefore, PhS based samples have roughly 3.7 times less photoactive material than that from standard cells. Fig. 4a shows the *I*/*V* characteristic for both the reference and the PhS based solar cells. All parameters that determine the solar cell characteristics as the current intensity in short circuit (I_{SC}), the open circuit voltage (V_{OC}) and the filling factor are much better in the case of the PhS topology. PhS architecture improves the total efficiency value of dye sensitized PES cells by a factor of 5. Fig. 4b shows the spectral response of both cells. One can see that PhS electrodes induce a large amplification of the photocurrent in the whole range of the cell response (300–800 nm). However, the amplification effect is more important in the optical region where titania is active (see peak around 350 nm). At the absorption edge of titania, the refractive index value increases and consequently, light scattering effects are enhanced. As the processing method for both types of samples is identical, we infer that the much higher efficiency in PhS electrodes can only be ascribed to the different topology of the titania network.

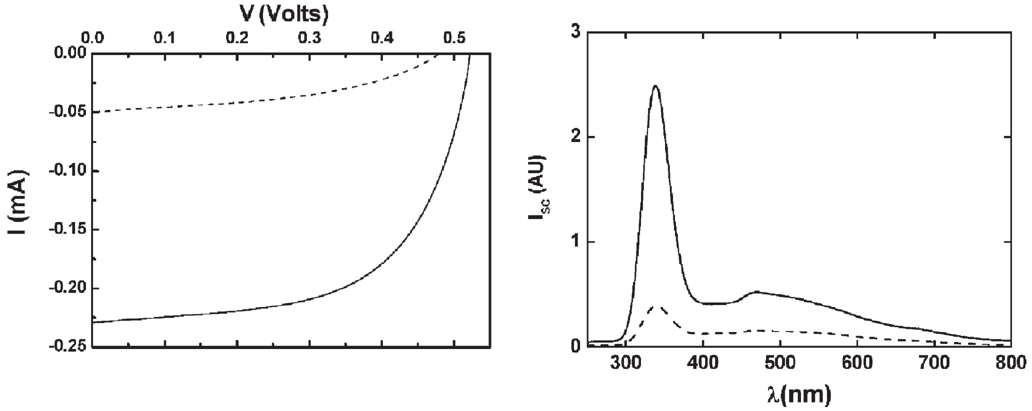

Fig. 4 (a) *I*/*V* characteristic of dye sensitized PES cells under AM 1.5 conditions, and (b) Photocurrent spectra for standard (dashed line) and PS (continuous line) titania electrodes.

Finally, it is worth pointing out that PES cells as described above present very low efficiency values (below 1% for the PhS cell). Although it is beyond the goal of this communication to describe in detail the strategy to improve the efficiency of the PhS based solar cells, we would like to comment on the main issues to be addressed. Very low efficiency values are reached because a modified synthesis method has been followed, different to that usually employed for the well known high efficiency titania based PES cells.[17] A standard recipe has been carried out, but using higher pH values (pH = 3), compatible with the colloidal template. Otherwise, the PhS template collapses, and the inverse Apollony architecture cannot be obtained. The efficiency problem could be solved, either by investigating other gentler synthesis routes or by using more robust templates. Also, we should increase the percentage of active Ru dye linked to nanoparticles. This is a very important step because the PhS network is highly porous and the density of the active material is about four times smaller than for standard electrodes. Therefore it would be necessary to find a compromise between a high efficient scattering cross section and a suitable proportion of active material.

In conclusion, we have shown a PhS architecture capable to trap light very efficiently in the near UV and the whole VIS regions. Also it can be applied to harvest efficiently photons in dye sensitized PES cells. This new topology can be useful for preparing efficient PES cells.[18]

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