

SUPPLEMENTARY INFORMATION (MS B613422J).

Introduction: The term PhS was first introduced by A. Lagendijk¹ (NATO School on Photonic Crystals and Light localization in Crete, Greece, June 2000) referring to porous GaP obtained by electrochemical methods. Here, our concept of PhS concerns a collection of random air nano and microcavities in a high dielectric medium formed by nanocrystals of Titania. Apollony fractal packing is the best way to efficiently pack spheres of different sizes. It has fractal dimension of 2.7^2 . In our case we have constructed the inverse topology formed by spherical cavities in a high refractive medium of TiO₂ nanoparticles (see PhS samples fabrication method).

PhS samples fabrication method: Our PhS samples have been fabricated using the templating methods like those to fabricate inverse opals³. The topology consists of spherical air cavities in a high refractive medium of TiO₂ nanoparticles. The fabrication method makes use of thin films (with thickness values between 6 and 50 micrometers) templates made of polydisperse latex particles. Thin films are deposited on transparent electrodes made of Indium Tin Oxide (ITO) with a method similar to that used to grow colloidal crystal thin films⁴. We have used monodisperse latex spheres of 1500, 400, 300 and 150 nm, with a proportion of 82:12:4:2 respectively, to favor Apollony packing. Also, those particle sizes can template spherical cavities with different diameter values, where all photons, from the UV, VIS and near IR regions, can strongly resonate within them. Particles suspension, (in a concentration of 10% in weight) was firstly sonicated for about 10 minutes. In order to induce the fractal ordering we have settled the colloid very rapidly to avoid gravity induced particle separation.

TiO₂ particles (average diameter of 30 nm) were synthesized within the interparticle pores of the colloidal template by decomposition of Titanium Isopropoxide^{5,6} (Aldrich, 99,9%) in a dry box through several cycles of infiltration and temperature treatment (at 50°C).

SEM Characterization: The morphology of the samples was examined by scanning electron microscopy (SEM) with a JEOL 6300 microscope using an accelerating voltage of 20 kV. Samples were covered by a sputtered gold thin layer before imaging.

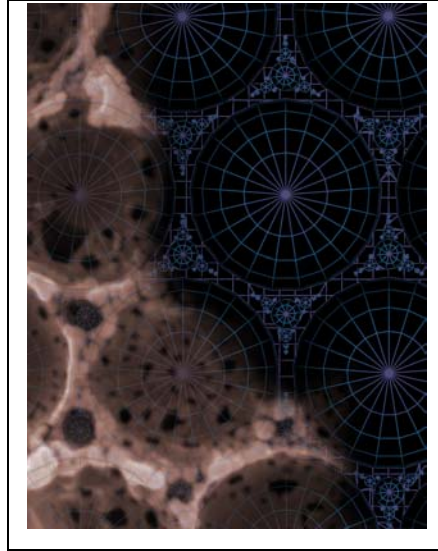


Figure 1S. Apollony fractal structure superimposed on a SEM image of the PhS

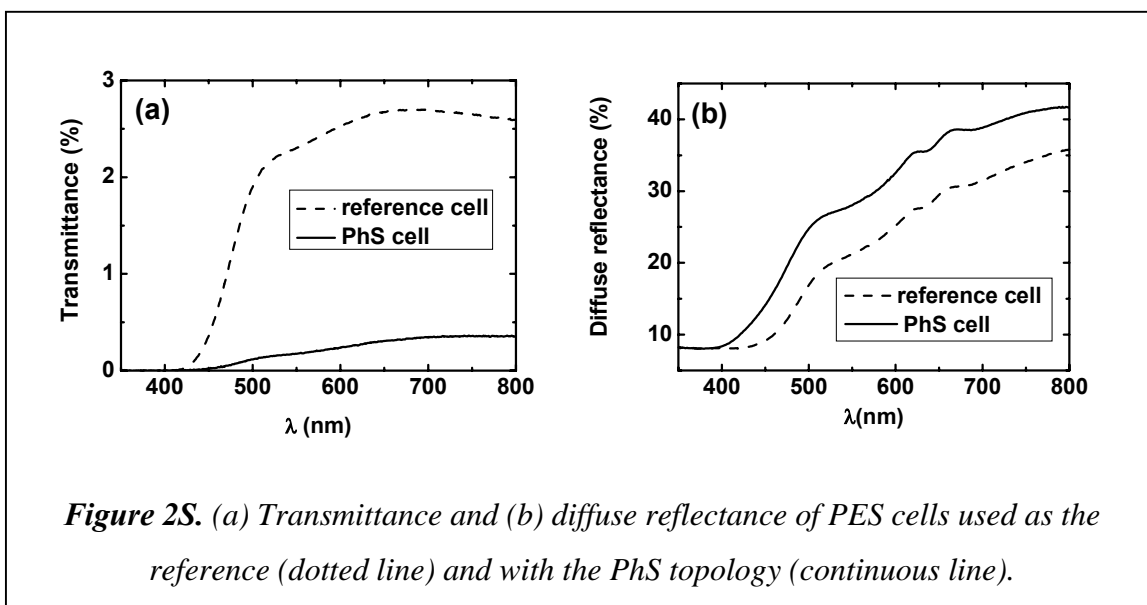
Figure 1S shows an artistic Apollony fractal structure superimposed on a SEM image of the Titania PhS. It shows small cavities at the intersection of three touching large cavities with close similarity to the Apollony packing model.

Optical properties: In strongly scattering systems, as the PhS samples we are concerned, it is customary to plot the reciprocal of optical transmittance (I/T) as the magnitude that represents the scattering intensity of the sample under study. The inverse of transmission is proportional to the optical mean free path (l) through the expression $I/T = L/l$, where L is the sample thickness. In this assumed that $l \ll L$, as it occurs in TiO_2 systems^{7, 8}.

From a naïve model one can estimate the mean value of the refractive index of a composite structure as⁹ $\langle n \rangle = ((n_1)^2 f + (n_2)^2 (1-f))^{1/2}$, where n_1 , n_2 are the refractive index for bulk Titania, and air respectively; f being the filling fraction of Titania nanoparticles. A simple calculation gives $\langle n \rangle = 1.30$ (for a PhS/air system with a porosity value of 85%). From the Fresnel formula for reflectance, $R = ((\langle n \rangle - 1)/(\langle n \rangle + 1))^2$, one can estimate a reflectance value, at the air/PhS interface, of $R = 0.13$.

However, as PES cells concern electrode/liquid systems, the refractive index contrast is different from the Titania/air system. Therefore, it is necessary to assess the optical properties of a real device. To facilitate optical experiments, the Pt electrode of PES cells has been removed. As both the solvent and the electrolyte are embedded in the Titania-dye network, one can perform optical experiments on the electrode/liquid free

surface. Figure 2S shows both the transmittance (Figure 2S(a)) and the diffuse reflectance (Figure 2S(b)) of a PES cell with a standard design (dotted line) and with PhS topology (continuous line). Both the reference and the PhS PES cells have a thickness value of 27 and 21 micrometers respectively. Several consequences can be extracted from the data. Firstly, as expected, PhS cell shows much lower transmittance (T) values than those of reference cell. Also, diffuse reflectance (R) is roughly similar for both samples. Therefore absorbance (A) defined as $A=1-R-T$, shows much larger values for the case of the PhS sample. Secondly, as in the case of Titania/air system (see Figure 3), PhS cells show a transmittance value (normalized to its thickness) one order of magnitude smaller than that of the reference cells. One should expect smaller scattering effects in electrode/liquid systems than those of the Titania/air interface. We do not have an answer to this unexpected result. Perhaps, the presence of Ru dye in the Titania network could modify the refractive index as usually it occurs when a heavy metal is incorporated in a dielectric material. In addition, refractive index of the Ru compound should be further enhanced in the visible range where the dye absorption is taking place.



Solar cell fabrication and characterization: The photoelectrochemical cell was made as following. The electrode is composed of nanoparticles of TiO_2 with PhS topology as described above. For the standard solar cell, we employed a paste of Titania nanoparticles synthesized according the same procedure as in the case of Photonic

Sponge. We have used a thickness of 23 μm for both PhS and standard Titania thin films.

Both samples were impregnated at room temperature, overnight, with 120mM of Ruthenium 620-1H3TBA (Solaronix) dissolved in ethanol.

The cell, with an active surface area of $0.5 \times 0.5 \text{ cm}^2$, was assembled by sandwiching a 50 micrometers thick Surlyn (Dupont) spacer between the inverse opal (or standard TiO_2) electrode and the counter electrode. The counter electrode was made by sputtering Platinum on an ITO substrate. The redox couple electrolyte solution consisted of 0.5 M of LiI and 0.05 M of I_2 with 0.4M of tert-butylpyridine. We have used methoxypropionitrile as solvent.

Solar cells characteristics were performed using a global AM1.5 filter in an Oriel solar simulator equivalent to a solar intensity of 1000 watts/m^2 .

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