

Inverse Opal Photonic Crystals as a Strategy to Improve Photocatalysis: Underexplored Questions

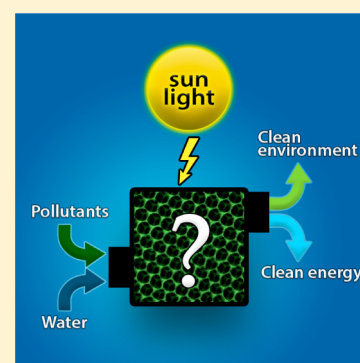
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ABSTRACT: The structuring of materials in the form of photonic crystals for photocatalytic applications is a quite new strategy aiming to enhance the performance of the photocatalysts at wavelength ranges where their absorption is poor. It is of particular interest to successfully manufacture an efficient photocatalytic system that could make use of solar light. Thus, the key of the strategy is the “slow photon effect”, occurring at the edges of a forbidden band for photons. In this Perspective we have chosen some questions that we consider of relevance and that are well worth being addressed both theoretically and experimentally. It is the aim of this discussion to eventually lead to a more productive use of inverse opals as photonic photocatalytic materials.



The ever growing energetic needs of the human population¹ have recently led to a vigorous growth of the interest in photocatalysis.² Several different strategies have, in particular, been explored to efficiently use solar light for photocatalytic reactions, with the focus being directed toward reactions for environmental remediation, disinfection, and energy production through water splitting.³ One of these strategies is to use photonic crystals⁴ to enhance light–matter interactions.⁵ Photonic crystals are composite materials in which the refractive index has a periodic variation, resulting in a band structure for photons analogous to the electronic band structure in semiconductors being a consequence of the periodic electric potential of the atomic lattice.⁴ Interestingly, this band structure predicts the propagation of photons with reduced group velocity, that is, *slow photons*, at certain crystallographic directions. Because lower values for the group velocity result in higher values of the absorption coefficient,⁶ photocatalytic processes should, in principle, be able to benefit from the slow photon effect through an enhancement of their light absorption capability at wavelength regions where the material absorbs poorly.

The photonic crystals mostly used for photocatalysis possess an inverse opal structure. This is a face-centered cubic (FCC) array of air spheres within a matrix of the respective photocatalytic material (Figure 1). The usual material's choice of preference is TiO_2 with the photocatalytic matrix of its three-dimensional periodic systems being formed of nanoparticles produced upon the hydrolysis of a titania precursor. Depending on the method of synthesis the particle size may vary. Figure 2 shows the band structure for photons of such a system, that is, a TiO_2 inverse opal.

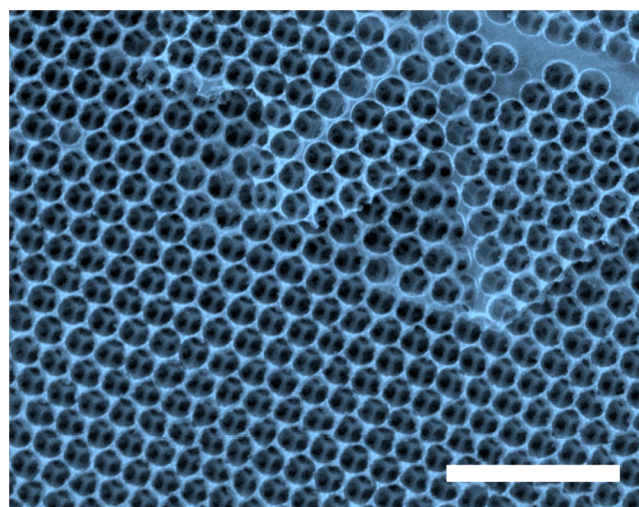


Figure 1. Field-emission scanning electron microscopy image of a TiO_2 inverse opal. Scale bar: 1 μm . The sample was fabricated by infiltrating titanium tetraisopropoxide into a polystyrene opal structure prepared by the capillary deposition method.⁷ The exposed crystallographic face is (111) oriented parallel to the substrate surface.

The band structure for photons in inverse opals (Figure 2a) shows two important features. The first, and most noticeable, is

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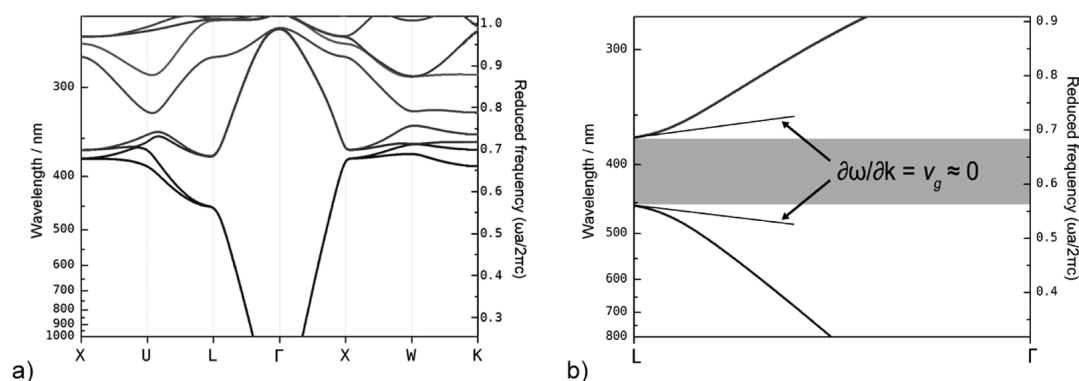


Figure 2. (a) Photonic band structure, calculated with the MPB software [The MIT-Photonic-Bands (MPB) is a freeware distributed by the Massachusetts Institute of Technology; Johnson S.G., Joannopoulos J.D. “The MIT photonic-bands package”. Available from: <http://ab-initio.mit.edu/mpb/>],⁸ for a TiO₂ inverse opal (refractive indices: $n_{\text{TiO}_2} = 2.5$ and $n_{\text{air}} = 1.0$). The wavelength scale shown on the left corresponds to a diameter of the spherical cavities of $D = 180$ nm, that is, a lattice parameter $a = D\sqrt{2}$ on the reduced frequency axis. (b) Detail of the band structure along the Γ –L direction in the reciprocal space, that is, the $[111]$ direction in real space, parallel to the normal of the surface. The stopband is indicated as a shaded region, and represents the interval of forbidden states for photons. The reduced group velocity for slow photons is also indicated schematically by approximate slopes at the edges of the stopband.

the existence of a photonic stopband, that is, a range of forbidden frequencies. Photons within this particular energy region cannot propagate through the crystal and are, consequently, reflected. Figure 2b shows a stopband for the Γ –L direction in the reciprocal space, which corresponds to the $[111]$ direction in the direct lattice, perpendicular to the (111) face.

This face is the commonly exposed surface and is obtained almost independently from the preparation method of the inverse opals. The stopband position depends on the incident angle of light thus explaining the iridescence of inverse opals, a property which lends a unique beauty to such structures. However, the fact that photons possessing a frequency within the stopband are reflected and not absorbed seemingly does not turn these systems into suitable photocatalysts, for which light absorption is a mandatory prerequisite. It will, however, be shown later that this particular reflection can be avoided, and may, rather than being disadvantageous, even become beneficial provided that a proper structural design is applied. The second important feature of the photonic crystal’s band structure is the flattening of certain photonic bands, in particular, of those close to the edges of the stopband. As the group velocity, v_g , is defined by the slope at any point, a flat band indicates a package of photons of a null or a low group velocity (Figure 2b). These photons are usually called “slow photons”. Herewith, the relevance for photocatalysis arises, because slow photon propagation enhances significantly the probability of absorption within the material.⁹ A suitable strategy therefore relies on the production of slow photons within the wavelength region where the photocatalyst absorbs poorly, leading to the generation of electron–hole pairs upon irradiation at these wavelengths.¹⁰ According to the electronic band gap of TiO₂, light absorption is maximal in the UV region, whereas it is already rather low at the blue side of the visible range, where sunlight, however, is more intense. Hence, TiO₂ inverse opal structures can be useful to extend the region of the TiO₂ light absorption into the visible part of the solar spectrum without the need of any chemical modifications of the photocatalyst.

The first detailed study concerning the slow photon effect for a photocatalytic reaction was published by the research group of Ozin in 2006.¹¹ Since then, a constantly increasing number of papers reporting photocatalytic processes employing photonic

crystals has been published. At a first sight, this shows that this new field of photocatalysis, that is, photonic photocatalysis, has definitively attracted many scientists to carry out investigations in this area. However, a deeper analysis of the available literature shows that, regarding the interplay between photonic crystals and photocatalytic reactions employing inverse opals, there is an imbalance of an overwhelming number of “scientific reports”¹² as compared to only a rather small number of “scientific publications”. Therefore, in the following, we will summarize and discuss questions that, in our humble opinion, still need to be clarified, better understood, and further explored.

In the seminal work by Ozin et al., the solid-state photocatalytic degradation of methylene blue over TiO₂ inverse opals was investigated.¹¹ The irradiation wavelength was selected to coincide with the absorption onset of TiO₂ (ca. 370 nm), and the wavelength where slow photons occur was tuned in and out of this region by preparing different samples with varying air sphere sizes. Thus, the position of the stopband and of the occurrence of the slow photons was found to shift in accordance to the corresponding lattice constant of the photonic structure (see Figure 2 and Figure 3a). The conclusion of this work was that upon irradiation with wavelengths matching that of the slow photons at the red edge of the stopband, a 2-fold enhancement can be attained for the solid state photodecoloration rate of methylene blue over the inverse opals in comparison to the photocatalytic activity of a “normal” nanocrystalline TiO₂ film (Figure 3b).

It was also shown that the reaction rate could be tuned by changing the incident angle of light, because the position of the stopband and of the slow photons strongly depends thereon. Moreover, employing white light irradiation ($\lambda > 300$ nm) a ca. 2-fold enhancement was also reported, even though the authors recognized that this situation involves the interplay of several factors and that its interpretation therefore is not trivial.

At Which Wavelengths Do Slow Photons in Inverse Opals Contribute to Photocatalysis? The positions of the stopband and of the slow photons (both principal photonic properties) require a perfect tuning (Scheme 1). On the one hand, if both are located within a region of strong absorption of the material (Scheme 1a), no photocatalytic improvement can be expected because both photonic properties vanish.¹³ On the other hand,

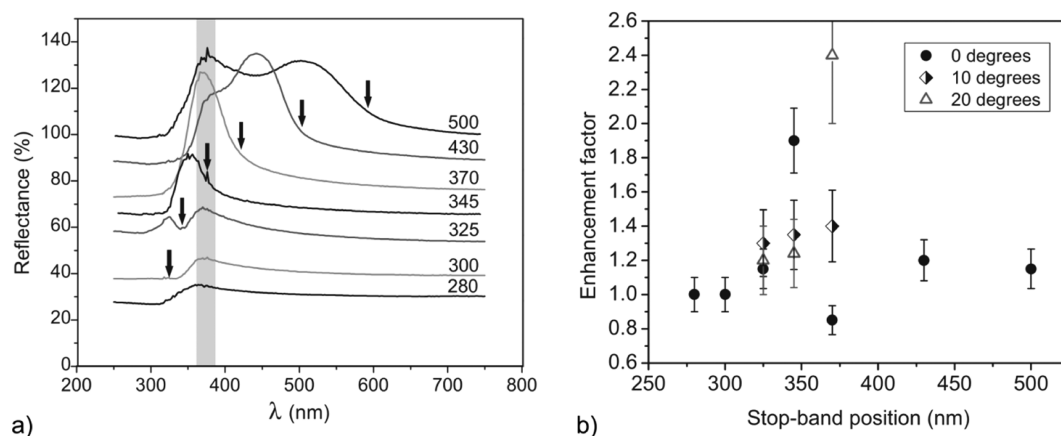
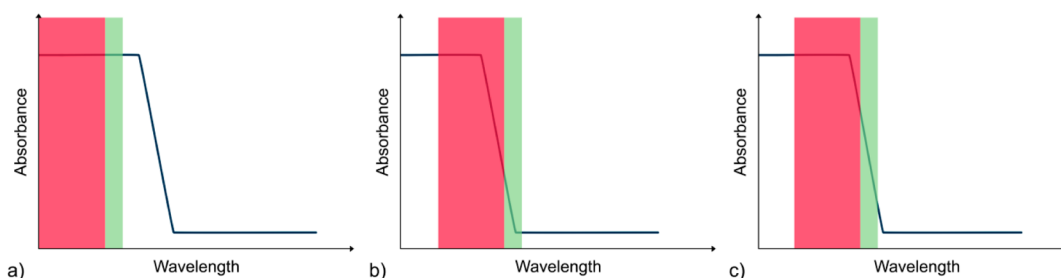


Figure 3. (a) Reflectance spectra of TiO_2 inverse opals prepared from polymeric spheres of different sizes. Different lattice constants yield a shift of the stopband, with the maximum reflectance indicated on the right, in nanometers. The shaded area shows the wavelength of the irradiation source used for the photocatalytic experiments. The black arrows indicate the expected region of the slow photon formation at the red edge of the stopband. (b) Enhancement factors (defined as the ratio of the methylene blue solid state photocatalytic degradation rate constant of each inverse opal to that of a nanocrystalline nonstructured TiO_2 layer) measured at different incident irradiation angles. Reprinted from ref 11 with permission from John Wiley and Sons.

Scheme 1. Strong Absorption of the Material Composing the Inverse Opal Can Suppress Both or at Least One of the Characteristic Photonic Properties: the Stopband in the Red Shaded Region and the Slow Photon Effect in the Green Region^a



^a(a) Stopband and slow photons are inactive. (b) Stopband and slow photons are active. (c) Stopband is inactive and slow photons are active; both are optimally positioned: the stopband reflection is avoided because it matches largely the strong absorption region, and the slow photon region is located where the material absorbs poorly. Therefore only in case (c) can the slow photons amplify the absorption of the material and contribute to the enhancement of the material's photocatalytic activity.

if at least one of both photonic properties are kept, the relative positions of stopband and slow photons are crucial to determine whether there is a photocatalytic enhancement or not. When both the effect of the stopband and that of the slow photons are active, the high reflectivity due to the stopband will hinder the photocatalytic activity because nonabsorbed photons will not be able to form electron–hole pairs. Thus, light losses due to the stopband reflection will dominate over the enhancement gained by slow photons (Scheme 1b). However, if the high reflectivity due to the stopband (or a large part of it) is avoided by strong absorption of the material, the slow photons will still be active producing electron–hole pairs thus contributing to the overall photocatalytic process (Scheme 1c).

Enhancements of photocatalytic activities measured in photonic systems are often explained assuming that slow photons at the red edge of the stopband are localized in the high dielectric material, that is, in TiO_2 , whereas those at the blue edge are localized in the low dielectric one (usually air or water). Localization of the electric field in the photocatalyst is expected to increase the material's absorption. However, several authors report absorption enhancements at the blue-edge of the stopband,^{10,15,16} in apparent contradiction with these localization arguments.

A theoretical model including defects (and light scattering originating therefrom) as well as more realistic experimental conditions should lead to a better understanding of these systems shining light on the physical chemistry of the underlying processes that are rather difficult to unravel by means of only experimental methods.

By means of theoretically calculated photonic band structures, for example, Figure 2, the frequencies (wavelengths) of the stopband and of the slow photons can be easily determined. However, predictions of these properties are not trivial for real samples. Defects in the photonic structure produce a broad reflectance band (stopband) superimposed on the reflectance spectrum of the material (Figure 3a). It is also a fact that an

incomplete infiltration with the photocatalytic material, that is, an inverse opal of a low density photocatalytic matrix, shifts the position of its stopband.¹⁴ Determination of the slow photon frequencies from experimental spectra entails a large uncertainty. In this sense, a reliable tool (experimental, theoretical, or a combination of both) to predict the spectral position of the stopband and the wavelength region of the slow photons in real inverse opals would definitively help to define and engineer the photocatalytic enhancement expected for any given periodicity of the refractive index contrast.

How May Theoretical Models Help to the Understanding of the Underlying Processes within These Systems? The theoretical bases for the photonic properties are usually derived under the assumptions of a perfectly ordered structure and zero (or very low) light absorption.³ It has, on the other hand, been shown that the photonic properties are almost entirely suppressed under conditions remote from the ideal perfect structure and from zero or very low light absorption properties.^{13,17} However, for their use in photocatalysis, the materials composing the inverse opal are definitely required to absorb light. Hence, any implementation of the photonic theory for photocatalytic applications that does not consider the photocatalyst's light absorbing properties raises questions concerning the validity of the model. Rigorous theoretical treatments of these systems taking into account the optical absorption of the photocatalytic material are, however, scarce. One example for such an approach is the work of Mihi and Míguez,¹⁸ who interpreted the enhancement achieved in dye-sensitized solar cells coupled to inverse opals by means of calculations based on the so-called scalar-wave approximation.

Another important factor in real photonic crystals is the presence of defects. Although their impact for the photocatalytic activity of photonic systems has been explored experimentally to some extent,¹⁹ a theoretical model including defects (and light scattering originating therefrom) as well as more realistic experimental conditions should lead to a better understanding of these systems shining light on the physical chemistry of the underlying processes that are rather difficult to unravel by means of only experimental methods.

Additionally, Mortensen et al. have shown,²⁰ by theoretical calculations, that the infiltration of photonic crystals with conducting electrolytes can smear out the photonic features. To the best of our knowledge, this effect has not yet been experimentally explored in appropriate photocatalytic studies employing inverse opals. The relevance of such findings for photocatalytic applications is high from the viewpoint of environmental remediation, for which real polluted samples are usually multicomponent solutions often with high contents of dissolved ions.

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Which Experimental Conditions Are Crucial to Guarantee a Slow Photon Effect? The results of investigations of the slow photon

effect will be extremely sensitive to various experimental parameters such as light scattering, porosity, or surface area, all of which demand a very careful experimental control. Light scattering within porous structures with²¹ and without^{22,23} any periodicity has been shown to enhance the light absorption capabilities of the photocatalyst and, therefore, cannot be easily disregarded as a factor determining the overall photocatalytic activity. Likewise, the use of polychromatic excitation (as employed in most experimental studies published to date) allows only a very qualitative identification of the slow photon effect, whereas a precise quantification is difficult because the number of electron–hole pairs generated by the absorption of slow photons is comparatively lower than the one produced by the natural absorption of the photocatalyst material (exhibiting, usually, high absorption coefficients).

The unambiguous identification of the slow photon effect is not a straightforward task with respect to the choice of the appropriate reference measurements. This is a challenging undertaking not only from the point of view of the irradiation source (vide supra) but also from the selection of the suitable reference material(s). Comparisons should include samples prepared from different sphere sizes to address the effect of different stopband positions. The photocatalytic performance of inverse opals may be compared to that of disordered structures of the same material where the porosity is similar but that do not exhibit any periodicity in the refractive index contrast. Normalization of the photocatalytic reaction rates with respect to the surface area should also be done. And the incidence angle of the light excitation is a parameter that must be clearly defined, since the achieved photocatalytic enhancement strongly depends on this angle, because the position of the stopband will be strongly dependent on the direction with which light propagates within the crystal (Figure 2).

Can the Slow Photon Effect Be Used in Suspensions Instead of Films? An interesting approach concerning investigations of photonic photocatalysis was presented by the group of Minero,^{24,25} in which inverse opal structures have been implemented not as a film but as suspensions of the powdered material. In these studies the rate of aqueous photocatalytic reactions over TiO₂ powders prepared from ordered and disordered templates were compared, using 254 or 365 nm irradiation. For samples prepared from polymeric spheres of an appropriate size, the enhancement of the respective photocatalytic activity obtained upon 365 nm light illumination is ascribed to the slow photon effect. In this case, the incidence angle is not unique, as the particles freely rotate in the suspension and expose different facets of the inverse opal structure to the incoming light. Since the slow photon effect strongly depends on the irradiation angle,¹¹ it is reasonable to assume that a broad distribution of incidence angles can only yield an average value much below the maximum possible slow photon effect.

How Does the Preparation Method of Inverse Opals Affect Their Photocatalytic Activity? For potential “real-life” applications of photocatalytic inverse opals, a comparison of the photocatalytic activity of samples using the same model compound but prepared by different methods will be crucial. The most commonly used protocol for the preparation of photocatalytic inverse opals consists of a three-stage process. First, a template is prepared from monodisperse spheres which, by self-assembly, form a FCC arrangement, or opal. Next, the photocatalytic material (usually pristine or modified^{26–31} TiO₂, although there are reports of photocatalytic studies employing inverse opals made from different materials such as ZnO,^{32,33} BiVO₄,³⁴

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β -Ga₂O₃,³⁵ Bi₂WO₆,³⁶ and ZnGa₂O₄³⁷) is infiltrated within the voids of the opal template. Finally, the infiltrated opal is treated, often thermally, to remove the template material and as a result, an inverse opal is obtained. Although many different preparation procedures have been published,^{5,38,39} ranging from fast and low cost to highly controllable but expensive, most of the papers dealing with photonic photocatalysis employ the vertical deposition method⁴⁰ for the self-assembly of polymeric spheres, and a sol-gel reaction as the infiltration procedure of the photocatalytic material.⁴¹ Moreover, there are examples in the literature showing that the material used for the opal template²⁵ (usually polystyrene or polymethylmethacrylate) and reagents used for its synthesis⁴² can considerably affect the properties and thus the photocatalytic activity of the resulting inverse opals. Besides the Slow Photon Effect, What Are the Benefits of Structuring Photocatalysts as Inverse Opals? Several interesting properties of inverse opals can also be used in technological approaches. For example, photoelectrochemical experiments showed an improved reactivity toward molecular oxygen in comparison with disordered arrays of pores.⁴³ Another interesting feature is that there is an almost linear dependence of the photocatalytic reaction rate on the irradiation flux when using TiO₂ inverse opals, while a much weaker dependency is found for nonstructured TiO₂.^{44,45}

One further important aspect of photonic photocatalysis is the different photocatalytic efficiency exhibited by these materials upon variations of the incidence angle of the incoming light. It has been shown that the selectivity of the photocatalytic oxidation of organic compounds over titania can be tuned by changing the frequency of photon absorption per particle.⁴⁶ Thus, inverse opals of photocatalytic materials have the potential to become excellent systems for the realization of setups that could make use of this phenomenon in a very easy way.

How Do Inverse Opals Compare to the Reference Material Evonik–Degussa Aeroxide P25 TiO₂ Regarding Their Photocatalytic

Activity? For the case of TiO₂ inverse opals, if the reference is the nonstructured photocatalyst material, a fair comparison of their photocatalytic activity may be done using the commercial product Evonik–Degussa Aeroxide TiO₂ P25 as the standard photocatalyst, a widely employed photocatalyst with proven high photocatalytic efficiency for the degradation of many compounds.⁴⁷ In this sense, the best photocatalytic rates achieved with noncommercial but self-synthesized TiO₂ inverse opals so far are usually in the same order as those of P25 titania,^{25,42,45} whereas higher rates than those of P25 are more easily achieved by using modified TiO₂ or other photocatalytic materials.^{35,37,48–52}

We note that a proper comparison between photocatalytic materials should ideally be done on the basis of quantum yields.⁵³ However, due to the highly scattering nature of this type of samples it is very challenging to measure the absorbed light intensity. The measurement and comparison of *apparent* quantum yields, based on ISO standards such as the NO_x⁵⁴ or the acetaldehyde⁵⁵ oxidation tests, could offer a viable alternative.⁵³ *What Is the Maximum Surface Area Achievable in Inverse Opals without Compromising Their Photonic Properties?* Typical surface area measurements for TiO₂ inverse opals range from 10 to 60 m² g^{−1}, Table 1. Calculations based on geometric considerations of the inverse opal structure yield values slightly lower to those reported and predict an inversely proportional relationship between the surface area and the air sphere diameter. A considerably higher surface area, in the range 90–300 m² g^{−1}, can be achieved by preparing mesoporous inverse opals.^{56,57} However, an increase in porosity of the walls of the TiO₂ inverse opal structure produces two opposing effects. On the one hand, the increase of the surface area leads to a higher photocatalytic activity due to the larger number of surface sites available for reactions. On the other hand, the increase in porosity produces a decrease in the effective refractive index of the material, in detriment of the photonic properties of the system.¹⁴ Whether or not there is a maximum porosity without compromising the photonic properties of the inverse opals remains yet another open question.

Are There Alternative Architectures to Exploit Photonic Properties? An alternative approach for the use of photonic crystals was presented by Mallouk and co-workers.⁶¹ In their work, inverse opal structures have been employed in dye-sensitized solar cells where the light trapping and light absorption processes are separated in space as well as in different materials. Light trapping occurs when the inverse opal, acting as a mirror, localizes the electric field of photons within the stopband into a photoactive

Table 1. Surface Areas Reported for Anatase Inverse Opals Prepared with Different Air Sphere Sizes

air sphere size/nm	surface area/m ² g ^{−1}	comments	reference
130	11	Surface areas estimated from methylene blue adsorption experiments.	14
150	11.7		
180	12		
210	8.8		
201, 228, 315	60	A single value is reported but it is not clear to which sample type it corresponds. Samples are N- and F-doped.	30
200, 320	60	Both types of samples exhibit a similar surface area. Samples are decorated with Au.	58
125	18	Samples are decorated with Pt.	25
330	74	Samples are decorated with Pt. TiO ₂ is composed of ~57% anatase, ~36% rutile, and ~7% brookite.	59
200	50.6	Samples are N-doped.	
270	32.4	Values of 78.6 and 66.3 m ² g ^{−1} are obtained for TiO ₂ /Ta ₂ O ₅ and TiO ₂ /ZrO ₂ composites, respectively.	49
310	49	Values between 53 and 61 m ² g ^{−1} are obtained for samples decorated with CeO ₂ .	50
340	22	Samples are decorated with Au.	60
500	5–10		48

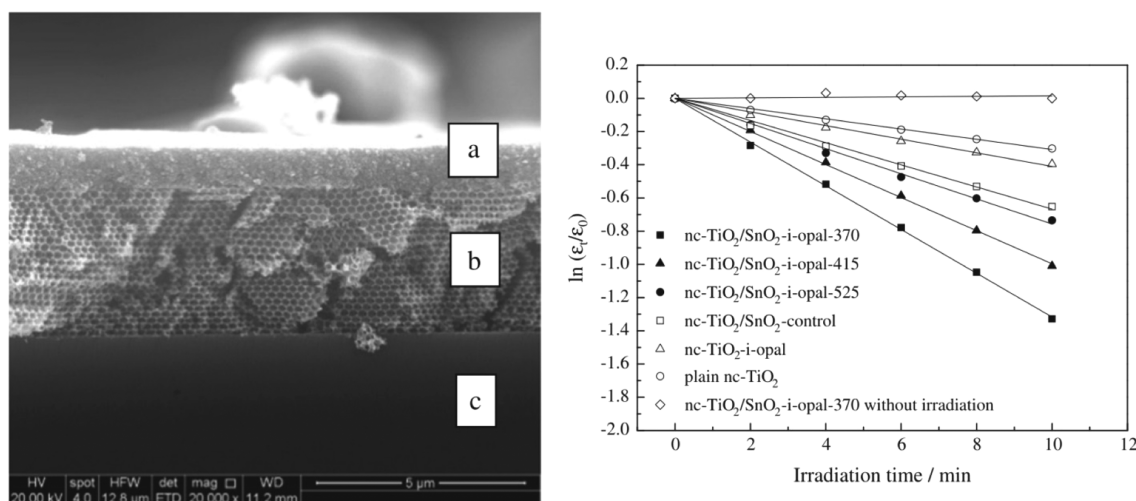


Figure 4. On the left: (a) SEM image of a nanocrystalline TiO_2 layer, (b) attached on a SnO_2 inverse opal, (c) on a quartz substrate. On the right: Kinetic profiles for the solid state degradation of Rhodamine B using TiO_2 / SnO_2 composites prepared from different polymeric spheres. The reference is a disordered template (control). A 150 W white-light Xe lamp was used as the irradiation source. Reprinted from ref 62 with permission from Elsevier.

material. Light absorption takes place on the latter material being prepared as a thin layer attached to the inverse opal. Employing this experimental approach an enhanced interaction time between matter and radiation could be achieved.⁶¹ As the slow photon effect, by definition, is only achievable within a narrow wavelength region, the advantage of this type of construction is that the light to be trapped, defined by the stopband, corresponds to a much wider wavelength region. An application of this concept to a photochemical reaction was presented recently by Chen et al.⁶² using a SnO_2 inverse opal and a thin nanocrystalline TiO_2 layer (Figure 4). When the onset of the titania absorption coincided with the stopband of the underlying SnO_2 inverse opal, an enhancement in the Rhodamine B degradation rate was found under white light irradiation. It must be noted that no experiments in the absence of TiO_2 are shown in this work, and thus, the reaction cannot be unambiguously labeled as photocatalytic.

Challenges and Future Opportunities. As a matter of fact, it must be said that until today, and to the best of our knowledge, it seems to be difficult to prepare photocatalytic inverse opals exhibiting all of the required properties, that is, very good optical characteristics, high photocatalytic activity, and mechanical stability. Without any doubt, the development of better preparation methods for inverse opals yielding large area samples with a low density of defects, while still being economically feasible, will place this research area closer to the theoretical limit of the slow photon enhancement. Concerning the latter aspect, more advanced theoretical models will most certainly help to identify: the optimal conditions necessary to make use of this effect, the wavelengths at which the slow photon effect is actually operative, and a reliable quantitative prediction of the absorption amplification by the material. To date, all of these issues remain as central questions in the area of photonic photocatalysis.

The focus of this branch of photocatalysis, that is, photonic photocatalysis, therefore lies on the effect of the slow photons that should enhance the production of electron–hole pairs. A futuristic view, in our opinion, places detailed explorations of the combination of this strategy with other approaches aiming to reduce charge carrier recombination as a key point along the

way that will eventually lead to the development of new materials with a high efficacy and efficiency in light to chemical reaction conversion processes.

Besides the commonly used inverse opals as photocatalytic films, novel architectures implementing photonic properties will also be of interest. Bilayer structures combining inverse opals with photoactive layers constitute one possibility, but we believe that also others, such as 1D photonic crystals, multiple inverse opal layers, and structures with engineered defects, hold promise for photocatalytic applications.

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Although photonic photocatalysis is still a young field of research, photocatalytic photonic crystals have already revealed their notable potential. So far, the background of the involved research teams, that is, traditional photocatalysis, undoubtedly has been of capital importance for most investigations published to date. As photonic photocatalysis calls for the multidisciplinary joint work of scientists and technologists, additional contributions from theory and engineering are considered to be essential ingredients for future research to advance at a deeper understanding of the very complex systems and to finally achieve their

implementation in “real life”. With the final goal being the development of highly efficient photocatalysts the likelihood that at least one road leading there will involve systems employing photonic crystals is according to our judgment rather high.

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Notes

The authors declare no competing financial interest.

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