

Standing Wave Enhancement of Red Absorbance and Photocurrent in Dye-Sensitized Titanium Dioxide Photoelectrodes Coupled to Photonic Crystals

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Abstract: The light harvesting efficiency of dye-sensitized photoelectrodes was enhanced by coupling a TiO₂ photonic crystal layer to a conventional film of TiO₂ nanoparticles. In addition to acting as a dielectric mirror, the inverse opal photonic crystal caused a significant change in dye absorbance which depended on the position of the stop band. Absorbance was suppressed at wavelengths shorter than the stop band maximum and was enhanced at longer wavelengths. This effect arises from the slow group velocity of light in the vicinity of the stop band, and the consequent localization of light intensity in the voids (to the blue) or in the dye-sensitized TiO₂ (to the red) portions of the photonic crystal. By coupling a photonic crystal to a film of TiO₂ nanoparticles, the short circuit photocurrent efficiency across the visible spectrum (400–750 nm) could be increased by about 26%, relative to an ordinary dye-sensitized nanocrystalline TiO₂ photoelectrode.

Introduction

Since the pioneering work of Grätzel and co-workers,¹ dye-sensitized photoelectrochemical cells have attracted much attention as inexpensive and relatively efficient solar photovoltaic devices. In these cells, a nanocrystalline titanium dioxide layer dramatically improves light harvesting, relative to a nonporous electrode, because its surface area is approximately a thousand times higher. Sensitizer dyes that were initially developed achieved almost unit current efficiency, but only at wavelengths shorter than about 550 nm. More recently, many different dyes have been investigated in order to extend the spectral response of the Grätzel cell, especially to wavelengths longer than 700 nm.² Dyes with increased red absorbance would allow for thinner TiO₂ layers, which would result in lower charge recombination and higher overall efficiency. Unfortunately, dyes with strong red absorbance also tend to have lower excited-state excess free energy, and this limits their usefulness.

Our approach to enhancing the red response of the Grätzel cell is not based on altering the dye, but rather on confining photons to the high refractive index dye-sensitized TiO₂. It has

been pointed out³ that a two-layer structure consisting of submicron spheres and a nanoparticulate TiO₂ layer should have enhanced light collection because of multiple scattering. We find that this prediction is correct and, in addition, now show that there is a novel enhancement effect that arises from the slowing and localization of light in the high index portion of the photonic crystal. If this high index material consists of dye-sensitized TiO₂, and if the photonic crystal is integrated into a bilayer TiO₂ nanoparticle structure, then the red response of the photoelectrode is markedly enhanced.

Light propagates at “the speed of light”, which in ordinary materials is in the range of $(1-3) \times 10^8$ m/s. This means that it takes about one hundred femtoseconds for light to traverse a medium of 10 μ m thickness. However, if light is confined to the same medium (for example, by Bragg scattering or Anderson localization),⁴ then its effective velocity decreases. Bragg scattering in a three-dimensional colloidal crystalline array was first observed with polystyrene colloids by Asher and co-workers in 1984.⁵ They discovered that stop bands in these arrays could be used to reject light of certain wavelengths. The idea of a three-dimensional photonic band gap crystal, in which light could not propagate in any direction within the material, was

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proposed by Yablonovich in 1987.⁶ Photonic crystals have three extraordinary properties: (1) prohibition of the propagation of particular wavelengths of light (the photonic band gap), (2) birefringent and anisotropic dispersion and (3) nonlinear dispersion. Low threshold lasers,⁷ waveguide structures that cause light to curve at acute angles,⁸ and perfect dielectric mirrors,⁹ are derived from the first property of photonic crystals. Reflective polarizers,¹⁰ and optical wave plates,¹¹ are proposed to use the second property. One of the effects that is derived from the third property is the so-called superprism phenomenon.¹²

The third property of photonic crystals, in which the group velocity of the light becomes anomalously small near the wavelength of a stop band, can be understood by considering the dispersion curve (E vs k) of light in a periodic dielectric.^{8,13} Approaching the stop band from the long wavelength side, light can be described increasingly as a standing wave. On the red edge of the stop band, the peaks of this wave are primarily localized in the high dielectric part of the photonic crystal, and on the blue edge, they are localized in the low dielectric part, as illustrated in Figure 1. This situation is analogous to that of an electronic semiconductor, where the wave functions for states just below (top of the valence band) and just above the band gap (bottom of the conduction band) are standing waves with the same periodicity but with a charge density that differs in position; namely, the charge density is localized either between or on the atomic sites. The fact that light waves are localized in different parts of the structure, depending on their energy, implies that an absorber in the high dielectric medium should interact more strongly with light at wavelengths to the red of the stop band, and less strongly to the blue. Effectively, the red part of the spectrum of this absorber will “borrow” intensity from the blue part. This spectral effect has previously been observed in X-ray scattering, where it is known as the Borrmann effect,¹⁴ and very recently was found by Wei and Asher¹⁵ in their studies of the plasmon resonance spectra of silver nanoparticles in silica colloidal crystal arrays.

To see if a similar standing wave effect could be used to increase the light harvesting efficiency of dye-sensitized TiO₂, we examined the optical properties of dye-sensitized photonic crystals and the photocurrent response of bilayer photonic crystal–nanocrystalline dye-sensitized titanium dioxide electrodes.

Experimental Section

Fluorine-doped tin oxide-coated conductive glass (TEC8, 8 Ω/sq.) was purchased from Hartford Glass Co., Indiana. These substrates were cleaned ultrasonically with water and 2-propanol, rinsed with water and then dried in an air stream. Titanium dioxide photonic crystals (inverse opals) were made by replica-

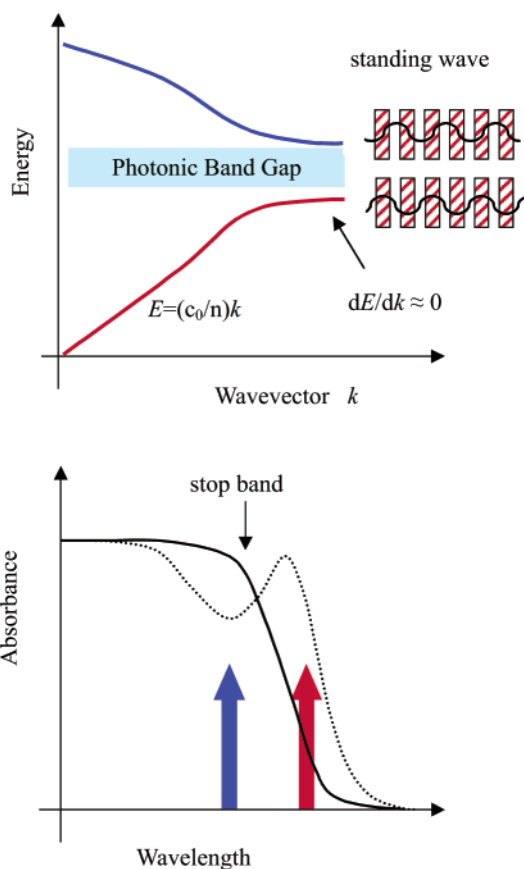


Figure 1. (Top) Simplified optical band structure of a photonic crystal. Near the Brillouin zone center light travels with velocity c_0/n , where c_0 is the speed of light in a vacuum, and n is the average refractive index. At photon energies approaching a full band gap or a stop band from the red side, the group velocity of light decreases and light can be increasingly described as a sinusoidal standing wave that has its highest amplitude in the high refractive index part of the structure. At energies above the band gap or stop band, the standing wave is predominantly localized in the low index part of the photonic crystal, i.e., in the air voids. (Bottom) Illustration of the effect of standing wave localization on dye absorbance. In an isotropic medium, the dye absorbs strongly in the blue but weakly in the red (heavy line). If the stop band is tuned to the position shown by the arrow, the blue absorbance is diminished and the red absorbance is increased when the dye is confined to the high refractive index part of the photonic crystal (dotted line).

tion of colloidal crystal (synthetic opal) templates.^{17–23} Mono-disperse carboxylate-modified polystyrene latex spheres (243 nm diameter) were purchased as a suspension from Seradyn Co. and used without purification. The suspension was diluted with 18.3 MΩ-cm deionized water to a concentration of 0.05 to 0.25 wt %. Colloidal crystals were prepared by a modification of the method of Jiang et al.²⁴ After the colloidal suspension was dispersed ultrasonically in a glass vial for 30 min., the substrate was immersed vertically. The vial was kept in an oven

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at 55 °C for 1 to 2 days until the suspension was fully evaporated, leaving a colloidal crystal film on the surface. Once dried, the diameter of the spheres in the colloidal crystal film was 215 nm.²⁵

To infiltrate titanium dioxide into voids of the template without destroying its periodicity, a liquid-phase deposition (LPD) method was used.^{26–31} The colloidal crystal films were first reacted for 3–5 min. with a 0.15 wt % solution of titanium isopropoxide in ethanol/0.015% HNO₃, dried vertically in air, and then soaked in an aqueous solution of ammonium hexafluorotitanate ((NH₄)₂TiF₆, 99.99%, Aldrich) and boric acid (H₃BO₃, 99.5%, Aldrich).²⁶ Uniform titanium dioxide films were grown from 0.1 to 0.3 M ammonium hexafluorotitanate and 0.2 to 0.5 M boric acid. The pH of the solution was adjusted to about 3 by adding hydrochloric acid.²⁸ By holding the sample in the solution at 50–70 °C for 10–30 min., it was possible to fill the void volume of the template completely with titanium dioxide. No shrinkage was observed during the process. The sample was rinsed with water and dried in air at room temperature. After the latex spheres were removed by calcination at 400 °C for 8 h, a highly ordered replica consisting of a mesoporous titanium dioxide framework with air holes was obtained. Powder X-ray diffraction patterns showed that the films were predominantly anatase TiO₂. To tune the position of a stop band precisely, we controlled the thickness of the titanium dioxide walls of the inverse opal in a second LPD step, which was performed after the latex spheres were removed. Thickness control was achieved by varying the duration of the second LPD step, as described elsewhere.²⁵

The samples were sensitized by soaking in a 3 × 10⁻⁴ M dye solution for 1 to 2 days. The sensitizer dye (RuL₂(NCS)₂: 2TBA, L = 2,2'-bipyridyl-4-4'-dicarboxylic acid, TBA = tetrabutylammonium) was purchased from Solaronix (Ruthenium535 bis-TBA, N719), and was dissolved in ethanol. The dye was desorbed in 3.8 M NaOH solution in order to quantify (by UV–visible spectroscopy) the amount adsorbed on the photonic crystal and the nanocrystalline titanium dioxide layers.

A conventional nanocrystalline titanium dioxide layer was applied to a 3 μm thick photonic crystal layer for photocurrent measurements. A titanium dioxide slurry was purchased from Solaronix (Ti–Nanoxide T, <d> = 13 nm). The slurry was applied to the photonic crystal layer by means of a squeegee, to give a total film thickness of 10 μm after drying on a hot plate at 80° for 10 min in air. The sample was then calcined at 400°C for 1 h, allowed to cool to ambient temperature, and then soaked in the dye solution for 1 to 2 days. Electron micrographs show that the TiO₂ particles applied by the slurry method do not penetrate significantly into the voids of the inverse opal layer. A conventional 10 μm thick nanocrystalline titanium dioxide film electrode was fabricated on conductive glass by the same method. The amount of dye adsorbed (0.127

μmol/cm²) was the same within experimental error on the bilayer and conventional electrodes.

The morphology and elemental composition of the samples were determined by scanning electron microscopy and by energy dispersed X-ray emission, respectively (EDX/SEM, JEOL, JSM-5400). The UV–visible transmission spectrum was measured with a diode array spectrophotometer (Hewlett-Packard, HP8452A) and the reflection spectrum was measured with UV/Vis/NIR spectrometer (Perkin-Elmer, Lambda 900 with home-made sample holder). Photocurrent was measured with a potentiostat (Bioanalytical Systems, BAS-100B/W) using a Xe lamp light source (Oriel Instruments, 6256, 150W) equipped with a monochromator (Oriel, Instruments, 77250). Samples for photocurrent measurement were made by sandwiching a 50 μm thick PET spacer between the colloidal crystal working electrode and a conductive glass counter electrode with a binder clip and placing in a 1 × 4 × 4.2 cm glass cuvette (Starna Cells, California). Iodide/triiodide electrolyte solution (Solaronix, Iodolyte TG50) was drawn up between the working and counter electrodes by capillary action. Incident light power was measured by a photopower meter (Ophir Optronics, Thermal surface absorbing head 2A-SH with NOVA-display). The electrodes were illuminated by monochromatic light (15 nm line width) from the nanocrystalline layer side. Short-circuit photocurrents (*I*_{sc}) were measured from 400 to 800 nm in 20 nm increments. The scan range was from -5 mV to +6 mV vs SCE.

Results and Discussion

The anatase form of TiO₂ is an n-type semiconductor with a 3.2 eV band gap,¹ meaning that it has no appreciable absorbance in the visible part of the spectrum. It also has a relatively high refractive index (2.5),¹⁶ which provides good dielectric contrast with air or common liquid electrolytes. Therefore, titania inverse opals should strongly diffract light at wavelengths near their stop band maxima. It is reasonable to expect an enhanced red response from dye molecules adsorbed on the TiO₂ nanoparticles that comprise such an inverse opal lattice, since the dye would be localized in the high refractive index part of the structure (Figure 1). The mesoporosity of the titania walls of the inverse opal is thus a key feature in using the standing wave effect to enhance the red response of the dye. Because porous titania made by the LPD process is less dense than crystalline anatase, its refractive index (2.25)²⁵ is slightly lower; however, this is still high enough to cause strong localization of red light on the dye/titania part of the structure.

Typical transmission and absorption spectra of titania photonic crystal films before and after dye adsorption are shown in Figure 2. These films were prepared in a single LPD step, and so the stop band maximum (486 nm) is to the blue of the maximum in the dye adsorption spectrum. The transmission is attenuated across the visible spectrum by the adsorbed dye, and is lowest in the blue where background scattering is high. By comparing spectra of dye molecules adsorbed to the two kinds of TiO₂ film (photonic crystal and conventional nanocrystalline TiO₂, bottom panel), it is apparent that there is a substantial enhancement absorbance on the red side of the stop band, as well as a slight attenuation of absorbance on the blue side of the stop band. The enhanced absorbance is most pronounced between 500 and 550 nm, but persists to a lesser degree to longer wavelengths.

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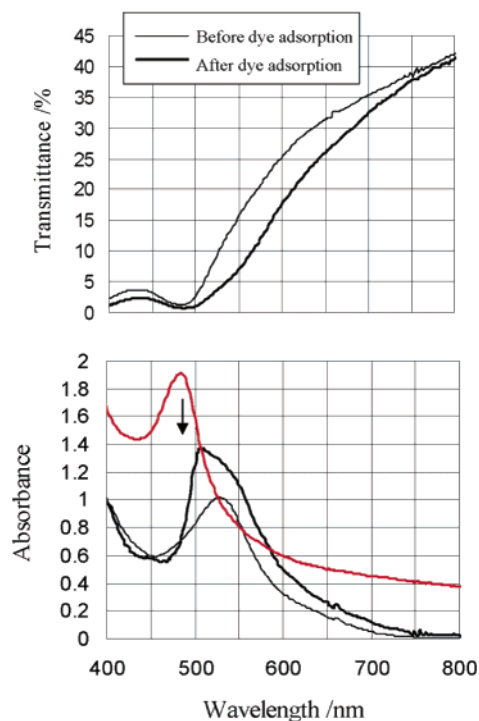


Figure 2. Top: Transmission spectra of a titania photonic crystal, prepared in a single LPD step, before (thin line) and after (thick line) dye adsorption. Bottom: Absorption spectra of the titania photonic crystal (red), the N719 dye adsorbed on the photonic crystal (thick line), and the dye adsorbed on a film of nanocrystalline TiO_2 (thin line). Spectra were taken in ethanol to provide a refractive index contrast similar to that of the liquid electrolyte used in the photoelectrochemical cell. The dye spectra in the bottom panel have the corresponding background (photonic crystal or nanocrystalline TiO_2 film) spectrum subtracted, and are normalized to the absorbance value at 400 nm. The position of the stop band at 486 nm is indicated by the arrow.

The effect of tuning the position of the stop band maximum on light absorption by the dye is shown in Figure 3. The absorption spectra of dye/photonic crystal samples are compared with the spectrum of the dye alone in ethanol solution. In each case, the absorbance is increased at the red edge of the stop band, relative to the dye in solution. This effect is particularly apparent in the bottom panel, where a substantial tail appears on the red side of the stop band.

Because dye adsorption has little effect on the absorbance of the photonic crystal at 400 nm, this wavelength was chosen for normalization of absorption spectra. These normalized spectra were then used to calculate absorbance ratios, as shown in Figure 4. The absorbance ratio (dye-sensitized photonic crystal relative to dye in solution) shows a suppression of absorbance for shorter wavelengths of light within about 100 nm of the stop band maximum. Dye absorbance is similarly enhanced at longer wavelengths. The ratio of normalized reflectance spectra shows a similar effect, but it is less dramatic than in the absorption spectra.

To investigate the effect of a photonic crystal in improving light harvesting efficiency, photonic crystals were combined with a conventional nano-crystalline layer. A cross-section of such a photoelectrode is shown in Figure 5. In this example, the photonic crystal is in contact with the transparent conductor. The bright layer below the photonic crystal layer in Figure 5 is a mesoporous TiO_2 film which grows during the LPD filling of the colloidal crystal. The thicker textured layer at the bottom of the image is the nanocrystalline TiO_2 film. Our attempts to

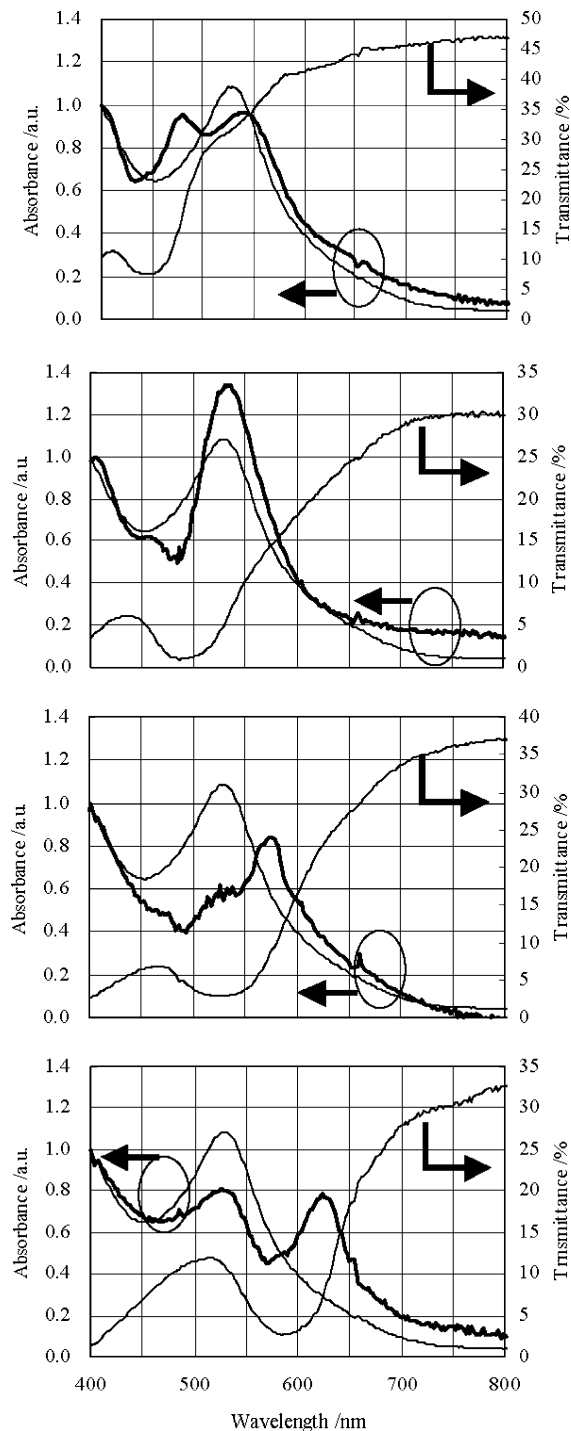


Figure 3. Absorption spectra of dye-sensitized photonic crystals (thick line) and the same dye dissolved in ethanol (thin line). The position of the stop band was adjusted by controlling the filling fraction of TiO_2 in the inverse opal, and moves progressively to the red from the top to the bottom panel. In each panel, a transmission spectrum is also shown to compare the position of the stop band.

fabricate bilayer electrodes with the nanocrystalline layer in contact with the transparent conductor were unsuccessful, because the conditions used in the LPD filling process caused this layer to delaminate from the substrate.

The wavelength dependence of the photocurrent in the bilayer cell was compared with that of a conventional Grätzel-type electrode of the same ($10 \mu\text{m}$) thickness, as shown in Figure 6. Between 400 and 530 nm, there was little difference between

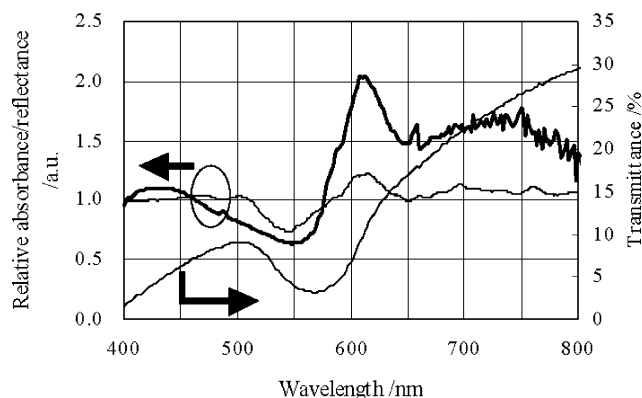


Figure 4. Relative absorption and reflectance spectral ratios. The absorption spectrum of the dye-sensitized photonic crystal was normalized by that of the dye dissolved in ethanol (thick line). The reflectance spectrum of the photonic crystal after dye adsorption was normalized to that before dye adsorption (thin line). The transmission spectrum is also shown to compare the position of the stop band.

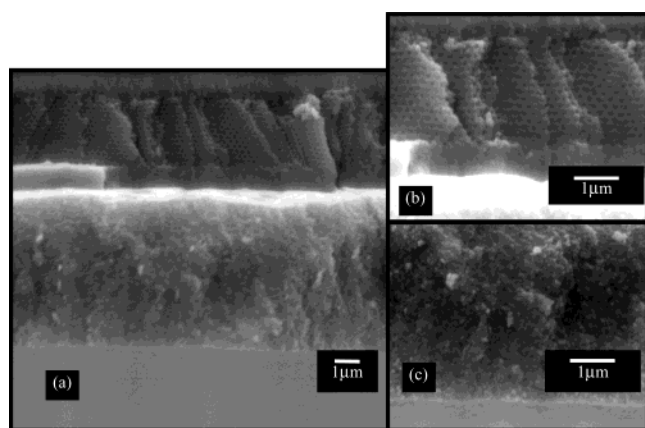


Figure 5. (a) Scanning electron micrograph of a cross section of the bilayer photonic crystal–nano-TiO₂ photoelectrode. The conductive glass is at the top of the image in (a). The photonic crystal layer and the nanocrystalline TiO₂ layer are enlarged in (b) and (c), respectively.

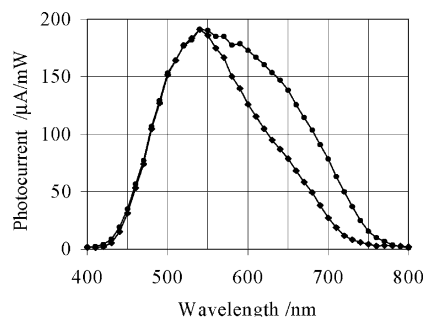


Figure 6. Wavelength dependence of the short-circuit photocurrent in the bilayer electrode (upper curve) and the conventional nanocrystalline TiO₂ photoelectrode (lower curve). The position of the stop band maximum in the bilayer electrode was 610 nm.

two kinds of electrodes. The close similarity in the maximum photocurrent from the two electrodes is consistent with the fact that both contain the same amount of dye. Between 540 and 750 nm, the short circuit photocurrent was substantially

increased in the bilayer electrode. The overall gain, integrated over the visible spectrum (400–750 nm), was about 30%.

Integration of the photoaction spectra, after multiplying them by the AM 1.5 energy spectrum,³² implies that the photonic layer should improve the short-circuit current in solar light by 26%. This improvement occurs without changing the thickness of the titanium dioxide film or the amount of dye adsorbed. It arises from multiple scattering (between about 550 and 650 nm), and from localization of light within the bilayer structure at longer wavelengths. The relative contributions of these two effects in enhancing the photoconversion efficiency are currently under investigation. We note that the suppression of absorbance on the blue side of the stop band does not affect the photocurrent, because the dye absorbance is very strong there.

These effects could be most profitably exploited in a geometry in which the nanocrystalline layer contacts the transparent conductor electrode, because in the Grätzel cell light normally enters the cell through that electrode. In the configuration used here, the photonic crystal layer is very reflective in the vicinity of the stop band, which leads to a substantial reflection loss using the normal illumination configuration. Also, in this configuration, there is substantial blue filtering by the electrolyte, which diminishes the photocurrent. We are currently working to fabricate electrodes in which the photonic crystal layer is deposited on top of the nanocrystalline TiO₂ layer to take full advantage of the properties of the photonic crystal.

Finally, we note that the spectral characteristics of the dye used here—strongly absorbing in the blue and weakly absorbing in the red—are fairly common for sensitizer dyes, semiconductor nanocrystals,³³ and organic thin film solar cells. This means that the same photonic crystal bilayer approach might be used to enhance the spectral response of those cells as well.

Conclusions

We have demonstrated that the slow group velocity of light in photonic crystals results in enhanced red absorbance of dyes confined to the high refractive index medium. The photocurrent of solar cells can be increased by coupling a photonic crystal to a conventional photoelectrode, and here the photonic crystal plays two roles: as a dielectric mirror for wavelengths corresponding to the stop band, and as a medium for enhancing light absorption on the long wavelength side of the stop band.

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