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Review of roles for photonic crystals in solar fuels photocatalysis

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Abstract. We cover the intersection of nanophotonics, materials such as photonic crystals (PC), but also irregular templated light scattering interfaces, with their application to solar fuels photocatalysis. We describe the fundamental principles of adapting nanophotonics to photocatalysis, particularly slow photon effects and how appropriate choice of stop band and edge position of the PC can be exploited for light harvesting. We also review several representative examples of nanophotonic design applied to photocatalytic semiconductor materials. We include the most heavily investigated photocatalytic materials (such as TiO_2), as well as inherently visible light active semiconductors, and materials sensitized with semiconductor nanocrystals or plasmonic metal nanoparticles. Finally, we review alternative scattering interfaces useful for improving the performance of solar fuels photocatalysis. © 2016 Society of Photo-Optical Instrumentation Engineers (SPIE) [DOI: [10.1117/1.JPE.7.012007](https://doi.org/10.1117/1.JPE.7.012007)]

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1 Introduction

1.1 Solar Fuel Photocatalysis at Semiconductors and the Challenge of Improving Light Harvesting

Direct solar water splitting is in principle one of the most sustainable pathways to produce clean fuels such as hydrogen (H_2) from cheap and abundant resources; however, the paucity of photocatalysts that efficiently drive water splitting under solar irradiation presently limits its viability as a route to renewable fuels. Functional photocatalysts must be cheap, stable in water, and able to perform the three fundamental functions in the photocatalytic process: (1) absorb solar radiation to produce reactive charge carriers (i.e., electron–hole pairs); (2) efficiently transfer charge carriers to reactive sites at the semiconductor surface while minimizing electron–hole recombination; and (3) drive chemical reactions of interest with high selectivity and yield of the desired product. Semiconductor photocatalysts with band edges satisfying the thermodynamic requirements for both water oxidation and water reduction, such as titania (TiO_2),¹ are limited by poor sunlight harvesting as a consequence of their large optical bandgap. Narrower bandgap semiconductors that absorb in the visible region, such as BiVO_4 and Fe_2O_3 , do not photogenerate the required thermodynamic potentials for water splitting.^{2–4}

Multiple strategies have been investigated to improve light utilization by wide bandgap semiconducting photocatalysts, with the most common including doping to shift band potentials, and sensitization with plasmonic metal nanoparticles, quantum dots, or dyes.^{5–7} Alternatively, the physical arrangement of the semiconductor can be controlled at the nanometer-to-micrometer scale to improve light harvesting. In the past decade, photonic crystals (PCs) of various morphologies have been investigated as a means of enhancing light utilization in semiconductor-based photocatalysts. We discuss below the recent trends in photocatalyst design that exploit

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the unique optical properties of PCs to improve sunlight utilization and highlight examples of how these photocatalyst structures are being used to enhance photochemical splitting of water.

1.2 Slow Photons and Photonic Crystals

To clarify how PCs can enhance photocatalytic processes, including H_2 generation, some background information on PCs and how they interact with light is necessary. Whether in pure or sensitized photocatalyst materials, the phenomenon characteristic of PCs that has been most commonly exploited to enhance light absorption in semiconductor photocatalysts is the “slow photon effect”—a slowing of light propagation in photonic materials at wavelengths near the photonic bandgap. PCs are ordered, periodic structures with alternating regions of high and low refractive index that satisfy Bragg diffraction conditions.^{8–11} A “forbidden band” of radiation with wavelengths on the same order as the periodicity of the PC structure cannot propagate through the PC, leading to a strong reflectance. The center of this band of radiation is known as the stop band or photonic bandgap. At the high- (blue) and low-energy (red) regions of the stop band, photons are multiply scattered in the lower refractive index and higher refractive index portion of the PC, respectively (Fig. 1),¹² thus effectively lowering the group velocity of light at the edges of the stop band.¹³ The propagation of slow photons increases their optical path length within the semiconductor or sensitizer and enhances the probability of generating charge carriers.

Although more exotic structures exist, inverse opals (IOs) are the most common PC structure utilized in photocatalysis. These structures are typically prepared by templating monodisperse polystyrene spheres in an opal arrangement and infiltrating the voids of the face-centered cubic (fcc) array with oxide precursors before removing the template by calcination^{12,14–18} (Fig. 2). The photonic bandgap (λ_p) for the IO films obeys a modified version of Bragg’s law

$$\lambda_p = 1.6D\sqrt{n_p^2 f + n_s^2 (1 - f)} \sin \theta, \quad (1)$$

where D is the diameter of the spherical voids in the fcc structure, f is the volume fraction of the spherical pore volume, n_p is the refractive index of the pore-filling fluid, n_s is the refractive index of the solid framework, and θ is the angle between incident light and (111) plane of the fcc structure.¹⁵ The exact frequency of the photonic bandgap is highly sensitive to the refractive indices of the solid and voids and will redshift as the refractive index of the pore-filling fluid increases (Fig. 3). The critical spatial dimension, D , is controlled directly during IO synthesis; the stop band is synthetically tuned as a function of the spherical template diameter (Fig. 4).¹⁹

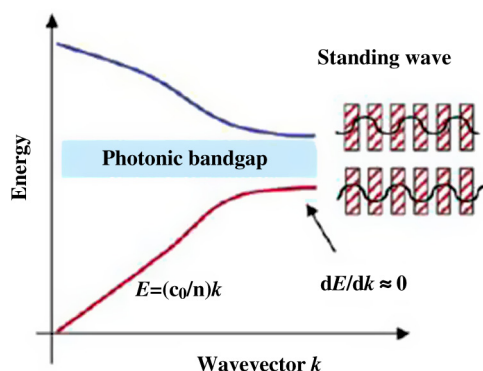


Fig. 1 Simplified optical band structure of a PC. At photon energies approaching a full bandgap or a stop band from the red side, the group velocity of light decreases and light can be increasingly described as a sinusoidal standing wave that has its highest amplitude in the high-refractive index part 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. Reproduced with permission from Ref. 12. Copyright 2003 American Chemical Society.

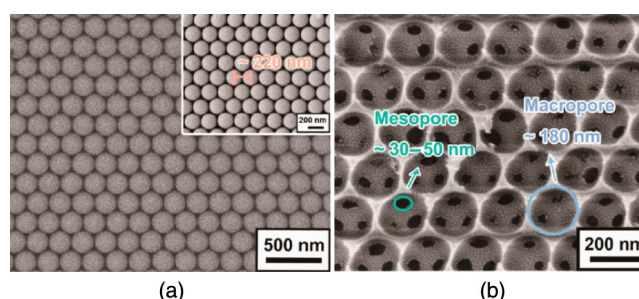


Fig. 2 Scanning electron micrograph (SEM) of (a) colloidal crystal template of polystyrene spheres (200 nm) and (b) three-dimensional ordered macroporous architecture of Mo:BiVO₄. Reproduced with permission from Ref. 18. Copyright 2014 American Chemical Society.

2 Coupling Photonic Crystals to Photocatalysis—Tuning the Red Edge of the Stop Band to the Photocatalyst Absorption Maximum

2.1 Tuning the Photonic Crystal Stop Band Around the Semiconductor Band Edge

Precise tuning of the stop band is necessary to exploit the slow photon effect for enhanced photocatalysis. Findings by Chen et al.^{20–22} established the ground rules for slow photon-enhanced photocatalysis. They applied anatase TiO₂ IO films with stop bands centered at wavelengths between 280 and 500 nm to the photocatalytic degradation of methylene blue under monochromatic UV radiation at 370 ± 10 nm.²⁰ The most photocatalytically active anatase PCs featured stop bands at 345 nm—not 370 nm—because it is at the red edge of the stop band that light is most substantially slowed in the high index material. Monochromatic light of wavelengths matched to the stop band does not propagate in the PC. Anatase IO films with stop bands at 345 nm had a low-energy edge coincident with the 370-nm illumination (near the anatase band edge), enabling them to enhance degradation rates by a factor of 1.9. PC films with stop bands at 370 nm rejected the incident radiation and were less catalytically active than nonphotonic nanocrystalline TiO₂ controls. As predicted by Eq. (1), the positions of the PC film stop bands were sensitive to the incident angle of radiation; tilt angles of 10 deg, 20 deg, and 45 deg substantially shifted the stop bands of all films, changing the films that were most photocatalytically active.

When white-light was used to irradiate the films, the order of the reactivity for the series of stop bands changed: PCs with stop bands at 300 nm exhibited the most photocatalytic activity enhancement (with an enhancement factor of 2.3 relative nanocrystalline TiO₂). Under polychromatic radiation, the effects of reflection compete with the slow light effect at PCs. The wavelengths at which reflection occurs comprise a larger portion of the stop band than those wavelengths at the edges of the stop band, at which the slow photon effects dominate. Thus, positioning the stop band directly at the absorption edge can result in diminished photocatalytic activity under broad spectrum illumination.²⁰ However, absorption by the dielectric material strongly diminishes photonic effects.²³ Thus, positioning the stop band at energies higher (shorter wavelengths) than the TiO₂ band edge enhances band-edge excitation and at the same time minimizes reflective losses occurring at wavelengths between the stop band and its high-energy edge.

2.2 Tuning the Photonic Crystal Stop Band Around Sensitizer Excitation Maxima

The rules for matching the red edge of the stop band to excitation energy apply to sensitized PCs as well, whether they are sensitized with dyes, quantum dots, plasmonic metal nanoparticles, or atomic dopants; slow photon edges—rather than the stop band itself—should be matched to absorption of the sensitizer, with care taken to avoid reflective losses from the stop band. For example, slow photon effects when carefully matched to the 550-nm absorption

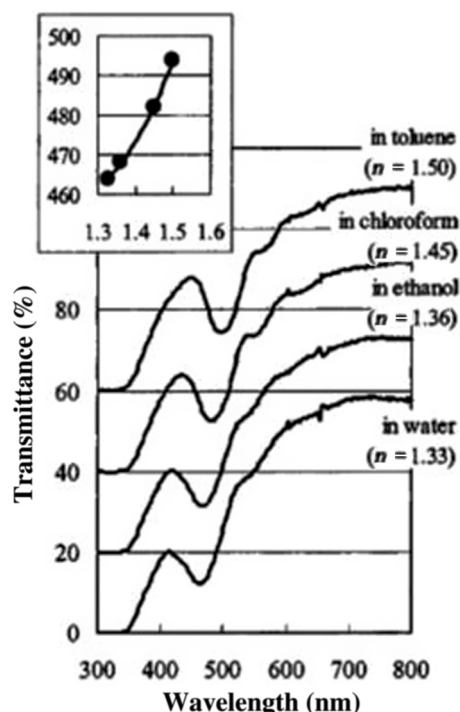


Fig. 3 Transmission UV-visible spectra of a TiO_2 IO structure with 169-nm voids and filled with solvents of different refractive index and insert showing band position as a function of refractive index of the void-filling solvent. The photonic stop band redshifts as the refractive index of the pore-filling fluid increases. The refractive index of the TiO_2 solid framework was estimated to be 2.40. Reproduced with permission from Ref. 15. Copyright 1999 American Institute of Physics.

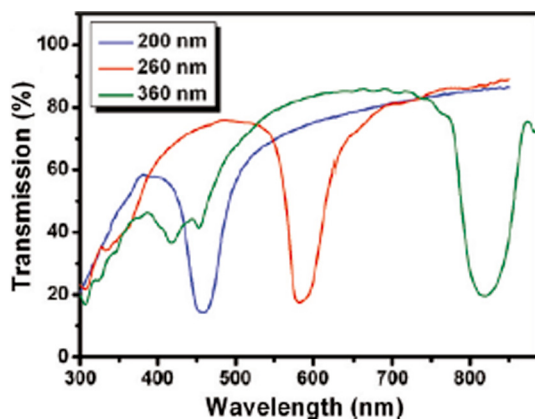


Fig. 4 Transmission spectra measured at normal incidence of opal structures deriving from three different polystyrene sphere diameters. Reproduced with permission from Ref. 19. Copyright 2011 American Chemical Society.

of Ti^{3+} -doped TiO_2 PCs enhanced the broadband visible light photocatalytic activity for methylene blue degradation by about a factor of 2 compared to the equivalently Ti^{3+} -doped nonphotonic counterpart; doped TiO_2 PCs with more poorly matched stop bands exhibited much more modest enhancement.²⁴

Curti et al.²⁵ prescribe some standard experimental guidelines that will help clarify the extent to which the slow photon effect is responsible for changes in photocatalytic activity. They recommend that the photocatalytic performance of IOs be directly compared to disordered

structures of the same material with comparable surface area and porosity to isolate the effects of surface area. Broadband excitation should be avoided to allow one to discriminate between photogenerated carriers originating from slow photons and those originating from normal bandgap excitation. Under these controlled experimental conditions, one can quantify the level of photocatalytic enhancement attributed to the slow photon effect and utilize the ground rules established in the seminal work by Chen et al.^{20–22} and others^{19,26} to engineer the stop band position for maximum photocatalytic activity.

3 Hydrogen Generation Photocatalysis at Photonic Crystals

Using the design principles described above, many researchers have exploited the slow photon effect to enhance H₂ generation by photochemical or photoelectrochemical water splitting in photocatalysts including TiO₂,^{27–30} WO₃,¹⁹ Fe₂O₃,³¹ Bi₂WO₆,³² and BiVO₄.^{18,33} (results and references are summarized in Table 1). At Pt-modified TiO₂ PCs,²⁷ the photocatalytic efficiency of H₂ generation as a function of the stop band position obeyed the same trends as those observed for dye degradation reactions by Chen et al.²⁰ The largest enhancement factor under broadband excitation of 2.5 occurred when the stop band was tuned to 342 nm—where the red edge overlapped the TiO₂ band edge.²⁷

While narrower bandgap alternatives to TiO₂ for photocatalytic water splitting^{2–4} may absorb more visible light, none features 100% photon-to-carrier conversion efficiency, and thus all can still benefit from improved light utilization. Alternatives to TiO₂ also suffer from drawbacks involving other parts of the photocatalytic process, such as valence/conduction band energies that are inefficient for water-splitting chemistry, and from fast electron–hole recombination kinetics. In particular, Bi₂WO₆ and BiVO₄ suffer from high bulk recombination rates and thus benefit from the shortened carrier path lengths to the semiconductor surface featured in the IO architecture.^{18,32–34} Nan et al.³⁴ show particularly strong enhancement factors of both surface-normalized photocurrents and photocatalytic oxygen and H₂ generation at the IO form of BiVO₄ (Fig. 5). While the red edge of the stop band in their BiVO₄ IO structures (~450 nm) overlaps well with the band edge of BiVO₄, their observed enhancement is probably due to more than the slow light effect alone. The simultaneous improvement of light management and electron–hole separation with IO forms of Bi₂WO₆ and BiVO₄ enhances photoelectrochemical water splitting relative to non-PC forms of the semiconductors to a significantly greater extent than that achieved when expressing TiO₂ in PC form (about 3× to 8× for Bi₂WO₆ and BiVO₄ compared to about 2× to 2.5× for TiO₂, Table 1). Note that while the improvement is more substantial in the PC forms of Bi₂WO₆ and BiVO₄, the overall photoefficiencies are still typically lower than that achievable with TiO₂.

Zhang et al.³³ compared the photoelectrochemical water-splitting activity of IO and planar Mo:BiVO₄ photoanodes. When the stop band was tuned to 513 nm, near the ~520-nm electronic bandgap of the oxide, photoelectrochemical activity was enhanced by about 8×. Photoelectrochemical activity was still enhanced—but to a much lesser extent—when the stop band was tuned to a frequency at which slow photons did not overlap the electronic bandgap excitation of BiVO₄. The enhanced activity in the absence of the slow photon effect is attributed to improved charge separation imparted by the PC architectures. Zhou et al.¹⁸ used transient photocurrent decay to measure the extent to which IO architectures enhanced charge migration during photoelectrochemical water splitting in BiVO₄ PCs. Carrier lifetimes were extended in BiVO₄ photoanodes with a macroporous IO structure compared to those observed in disordered films. The longest lifetimes were measured in IO structures containing both macro and mesoporosity; photoelectrochemical water-splitting activity was enhanced by roughly 3× to 7× in such films.

Mitchell et al.³⁵ applied a somewhat different approach to PC-enhanced photocatalysis, in which CdS nanocrystals (NCs) supported in a photocatalytically inactive zirconium oxide (ZrO₂) PC performed photocatalysis directly, instead of acting as a sensitizer. They observed a maximum ~5× enhancement for H₂ generation under visible light illumination relative to nonphotonic CdS/ZrO₂ at the “blue edge” of the PC stop band, suggesting that the supported CdS nanoparticles exploit slow photons in the lower-index voids in the PC—in contrast to the

Table 1 Diverse examples of photonic enhancement of photocatalytic and photoelectrochemical water splitting/H₂ generation reactions. Note that conditions that may impact the enhancement factor, such as excitation conditions, use of hole scavengers in reaction slurry/electrolyte, and photoanode bias in photoelectrochemical measurements, are omitted for the sake of brevity.

Material/ morphology	Reaction	Enhancement factor	Comment	Reference number
Pt/TiO ₂ IO	H ₂ generation in methanol:water	2.5	Slow photon enhancement of H ₂ generation photocatalysis	27
TiO ₂ and Au/TiO ₂ IO	Photoelectrochemical water splitting	2.07 without Au and 2.86 with Au	Slow photon enhancement and plasmonic enhancement	28
Pt/TiO ₂ IO	H ₂ generation in formate:water	<1 per surface area under UV excitation	Enhancement by IOs only observed at select excitation wavelengths; surface-area- normalized enhancement only marginally better than a disordered control	29
Ti ³⁺ -doped TiO ₂ NT array with top PC layer	Photoelectrochemical water splitting	10 under visible light	Combination of slow photon enhancement and visible light sensitization with dopant Ti ³⁺	30
α -Fe ₂ O ₃ nanoparticles deposited on graphene IO	Photoelectrochemical water splitting	1.4	Reduced electron-hole recombination and fast electron transfer	31
WO ₃ IO	Photoelectrochemical water splitting	~3 near excitation wavelength of activity maximum; >7 at low-activity wavelengths	Extensive angle-dependent study of slow photon enhancement; enhancement due to IO structure more pronounced at wavelengths where WO ₃ is initially less active	19
Bi ₂ WO ₄ IO	Photoelectrochemical water splitting	3	Slow photon effects and reduced bulk recombination	32
Mo:BiVO ₄ and Au-modified Mo:BiVO ₄ IO	Photoelectrochemical water splitting	8 over entire potential range; additional 55% increase with Au nanoparticles	Combination of slow photon enhancement, increased surface area and improved charge transfer, and SPR enhancement	33
Mo:BiVO ₄ IO	Photoelectrochemical water splitting	3 to 7, depending on electrochemical potential	Combination of cation-substituted composite oxide chemistry and PC-enhanced photocatalysis; control size of mesopores in addition to size of macropores	18
C quantum dots/BiVO ₄ IO	Photoelectrochemical water splitting	6	Combination of slow photon effects and visible light sensitization from C QDs	34
CdS/ZrO ₂ IO	H ₂ generation in methanol:water	4.7	CdS activity enhanced at blue edge of stop band of passive support	35
Au on TiO ₂ NTs array with TiO ₂ PC top layer	Photoelectrochemical water splitting	2.5 compared to sample with no PC top layer	Maximum enhancement when Au SPR matched to PC photonic bandgap	36
Au/TiO ₂ IO	Photoelectrochemical water splitting	2	Coupling of plasmonic TiO ₂ sensitization with slow-photon effects	37
Pt/TiO ₂ templated from butterfly wing	Photoelectrochemical water splitting	2.3	Enhancement of photocatalysis by aperiodic structure (unclear if enhancement is surface area or photonic effects)	38
N-doped TiO ₂ templated from leaf replica	Photocatalytic water splitting/H ₂ generation	3.3 to 8	Demonstration of viability of structural approach (unclear if enhancement due to surface area or photonic effects)	39

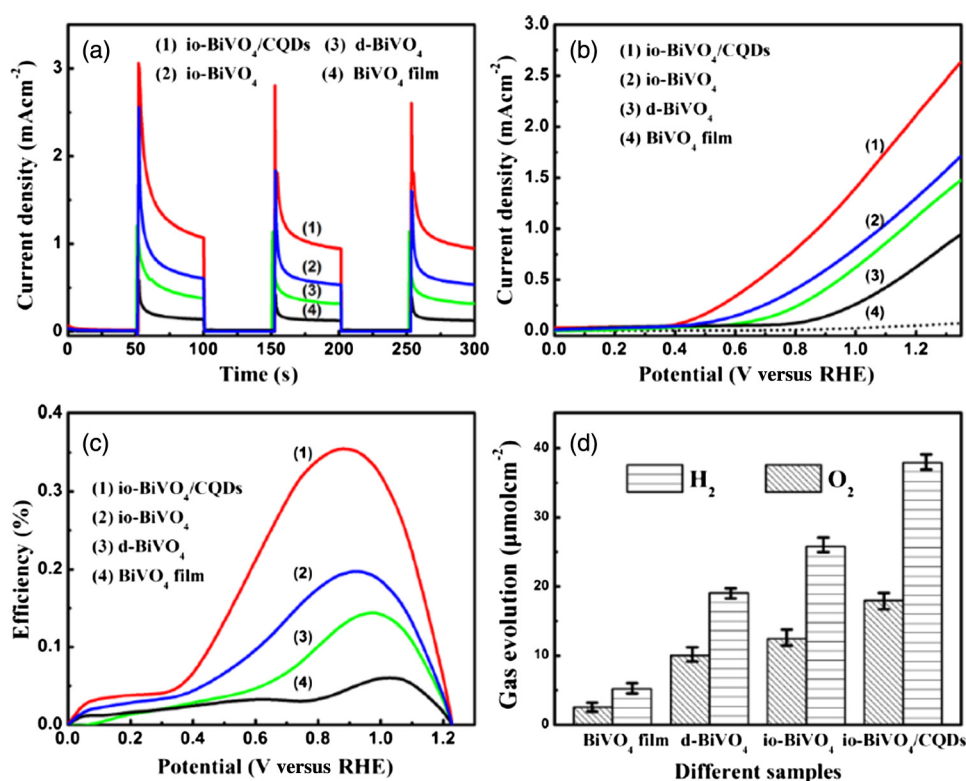


Fig. 5 Chronoamperometry measurements for (1) IO-BiVO₄ films modified with carbon quantum dots; (2) unmodified IO-BiVO₄ films; (3) Mo-doped BiVO₄ films; undoped BiVO₄ films. (a) Chronoamperometry measurements at an external potential of 0.9 V versus the reversible H₂ electrode (RHE) with repeated on/off cycles under UV/visible irradiation; (b) linear sweep voltammetry measurements at 50 mVs⁻¹ under UV/visible irradiation—the dashed lined represents the dark current of the undoped BiVO₄ film; (c) photoconversion efficiency as a function potential versus RHE; (d) surface-area-normalized H₂ and O₂ generation rates under UV/visible irradiation. Reproduced with permission from Ref. 34. Copyright 2015 American Institute of Physics.

case in which the PC support itself is photocatalytic. Their results—combined with the myriad results that demonstrate the opposite case in which the PC itself acts as the photocatalyst material and enhancement of photocatalysis occurs via localization of light coincident with the red edge of the stop band in the PC—convincingly demonstrate that the localization of the different band edges in PC-derived photocatalysts can be effectively tailored to application via materials design.

4 Combining Photonic Crystal Architectures with Plasmonics

Plasmonic metal nanoparticles, in particular Au and Ag, have recently received substantial attention as sensitizers for solar water-splitting catalysts due to their chemical stability and surface plasmon–resonant frequencies that overlap the solar spectrum.^{40–43} Whereas PCs improve carrier generation at or near the electronic band edge, plasmonic sensitizers can extend the useful range of photocatalysts much farther into the red (i.e., to lower energy, longer-wavelength radiation). Properly applied, the combination of PCs and plasmonic sensitizers enhances photochemical/photoelectrochemical activity to a greater extent than either strategy alone.^{33,36,37,44,45} For example, Zhang et al.³³ measured a roughly 26% enhancement in photoelectrochemical water splitting when they modified planar BiVO₄ films with ~20-nm plasmonic Au nanoparticles, but measured nearly 55% enhancement when they modified PC BiVO₄ with the same plasmonic Au nanoparticles. When plasmonic Au was present, the photocurrent response was extended beyond the electronic bandgap of BiVO₄ at 530 to 560 nm.

Analogous to other cases of combining photonics with sensitizers, the optimum enhancements from PCs + plasmonic sensitizers are achieved when the slow photon regions are positioned to overlap the surface plasmon resonance (SPR) frequency maximum while simultaneously avoiding reflective losses in electronic bandgap excitation.^{36,37,44,45} A large increase in optical extinction occurs when the slow photon region of a PC is well-matched to the SPR.^{36,37} Zhang et al.³⁶ coupled TiO₂ PC structures to TiO₂ nanotube (NT) arrays, creating TiO₂ NT/PC (NTPC) assemblies and subsequently deposited SPR-active Au NCs of different sizes onto the TiO₂ NTPCs. The intensity of the SPR response of Au NCs with SPR maxima well-coupled to the PC photonic bandgap was more strongly enhanced than those with more poorly matched SPR maxima (Fig. 6). The SPR-driven photoelectrochemical response (Fig. 7) and H₂ generation were similarly more strongly enhanced at the well-matched Au/TiO₂ NTPCs. Zhang et al.³⁷ achieved a maximum 2× enhancement in photoelectrochemical water splitting when the red edge of the stop band of PC TiO₂ was positioned at 518 nm, close to the SPR frequency maximum of the ~10-nm Au particles, but at a position where the photonic stop band (at 450 nm) would not interfere with bandgap excitation of the TiO₂. When the Bragg

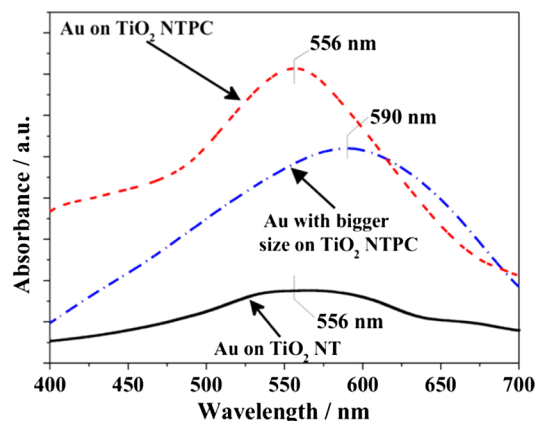


Fig. 6 Diffuse reflectance UV-visible absorption spectrum of Au NCs on TiO₂ NTs and the TiO₂ NTPC assembly (with a stop band centered ~552 nm) with the spectrum of TiO₂ subtracted for clarity of the Au SPR features. Reproduced with permission from Ref. 36. Copyright 2013 American Chemical Society.

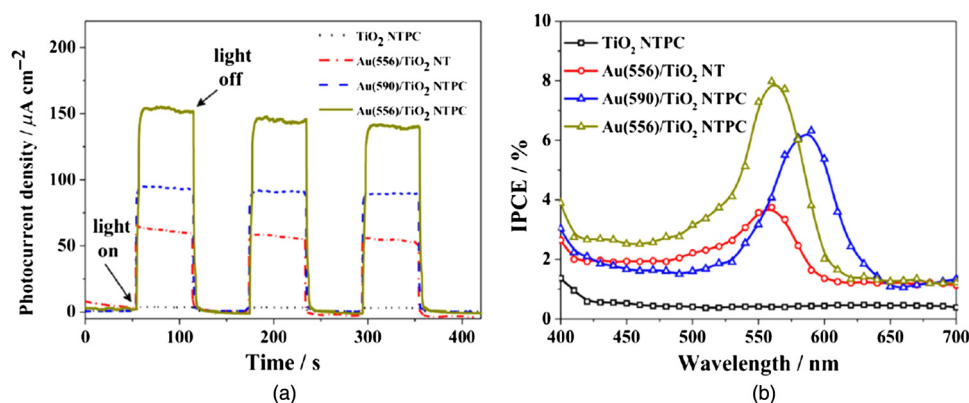


Fig. 7 Photoelectrochemical properties of the TiO₂ NTPC and Au/TiO₂ NTPC. (a) Amperometric $I-t$ curves at an applied potential of 1.23 V versus RHE under illumination of visible light with wavelength ≥ 420 nm with 60 s light on/off cycles; (b) incident photon-to-current conversion efficiency plots in the range of 400 to 700 nm at 1.23 V versus RHE. Reproduced with permission from Ref. 36. Copyright 2013 American Chemical Society.

reflection of the PC overlapped the Au SPR, the plasmonic enhancement was significantly suppressed.

5 Butterflies and Leaves: Alternate, Bioinspired, Photonic Crystal Geometries for Photocatalysis

Nature provides examples of structures that have unique interactions with light—whether they are naturally occurring PCs or disordered structures that multiply scatter light—that have inspired structural photocatalyst mimics. Butterfly wings^{38,46,47} and artificial leaves³⁹ have both recently been used as structural templates for photocatalysts. Butterfly wing-templated TiO_2 materials that feature regular, bicontinuous, gyroid structures with clear photonic bandgaps have been fabricated.⁴⁶

Although not a PC, the *Papilio helenus Linnaeus* butterfly wing contains structural elements that improve light utilization, including honeycomb-like hole arrays that multiply scatter light, “ridges” that guide light into the hole array, and a bottom reflective layer that recaptures light escaping from the honeycomb arrays. Platinum-modified TiO_2 replicas of *P. helenus Linnaeus* butterfly wings can function as H_2 -generating photocatalysts.³⁸ The wing-pattered photocatalyst strongly enhances ultrabandgap light absorption and shows a $\sim 7\times$ improvement in H_2 generation relative to nanoparticulate TiO_2 , although it was unclear how much of this enhancement could be attributed solely to surface area. Demonstrating the hierarchical possibilities of bio-structure-derived photocatalytic architectures, Yan and coworkers⁴⁷ deposited plasmonic gold nanorods onto bismuth vanadate (BVO) structures templated from wings of the butterfly *Papilio niri* (Fig. 8) and achieved substantial photocatalytic activity at red and near-infrared light illumination. Zhou et al.³⁹ replicated the hierarchical structure of *Anemone vitifolia* Buch leaves, which contain various components that serve to focus, scatter or guide light and enhance light-matter interactions. Using a two-step infiltration process, they produced an N-doped TiO_2 inorganic replica of the leaf structure that showed a roughly $3\times$ to $8\times$ enhancement in H_2 generation compared to nanoparticulate TiO_2 ; the activity was enhanced by another order of magnitude when modified with Pt nanoparticles.

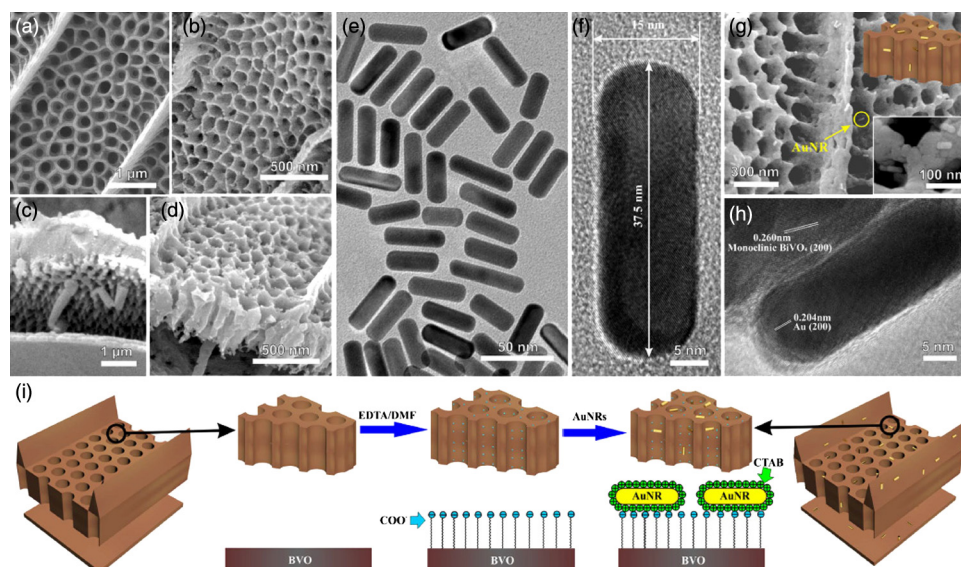


Fig. 8 SEM images of (a) top view of original *P. niri* wing scale, (b) top view of templated BVO replica of the *P. niri* wing scale, (c) cross section of the original scale, (d) cross section of the BVO wing, (e) TEM image of the gold nanorods (AuNR), (f) HRTEM image of a single AuNR, (g) AuNRs-loaded BVO wing with insets showing the simplified model (upper) and an enlarged image (lower), (h) HRTEM image of the AuNRs-loaded BVO wing, and (i) schematic diagram of the controlled assembly of AuNRs onto the BVO unit. Reproduced from Ref. 47 (open access). Copyright 2016 Nature Publishing Group.

6 Conclusions and Comments

Exploitation of the slow photon effect of photonic bandgap-containing materials requires rigorous matching of the red edge of the stop band with the desired excitation wavelength while avoiding absorption losses due to nonpropagation of light at the stop band. When PCs are correctly applied, photocatalytic activity enhancement factors of about 2 to 3 can be readily achieved, and in some cases enhancement of 5× or more may be possible. It is also possible to achieve light-utilization enhancement via the more disorganized process of internal light scattering, which is less demanding in structural precision, but also more difficult to design in a rational way.

A couple of important caveats should be mentioned. First, application of the slow photon effect to photocatalysis is illumination angle dependent, and as such can only be effectively applied in film geometries in which the illumination angle can be well-controlled. Practical photocatalysts are often used as fluid-dispersed (suspended) powders to maximize both mass transport and light utilization. The reactor geometry limitation inherent to PCs (i.e., a thin-film form-factor) means that careful consideration must be given to mass transport and light harvesting when designing the interfaces. Additionally, solar fuels photocatalysis involves many challenging photophysical and photochemical steps. Light harvesting is critical, but even with substantial improvements in light harvesting, many photocatalyst materials are still 2 to 3 orders of magnitude (or more)—rather than a factor of 2 to 3—from practical viability. One important class of solar fuels photocatalytic reactions omitted from this section involve reduction of carbon dioxide (CO₂) to hydrocarbons as its final step, rather than protons to H₂. Photochemical and electrochemical reductions of CO₂ comprise an enormous research challenge in its own right. Improvements on all photocatalytic fronts, however, continue apace; a number of composite solar fuels photocatalyst materials are approaching activity competitive with alternative routes to solar fuels and photonics could conceivably contribute enough additional efficiency to make them viable.

Acknowledgments

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