



Slow photon amplification of gas-phase ethanol photo-oxidation in titania inverse opal photonic crystals



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ABSTRACT

Here we describe the successful fabrication of six titania inverse opal (TiO₂ IO) photocatalysts with *fcc* [111] pseudo photonic band gaps (PBGs) tuned to span the UV–vis region. Photocatalysts were fabricated by a colloidal crystal templating and sol–gel approach – a robust and highly applicable bottom-up scheme which allowed for precise control over the geometric and optical properties of the TiO₂ IO photocatalysts. Optical properties of the TiO₂ IO thin films were investigated in detail by UV–vis transmittance and reflectance measurements. The PBG along the *fcc*[111] direction in the TiO₂ IOs was dependent on the inter-planar spacing in the [111] direction, the incident angle of light and the refractive index of the medium filling the macropores in the IOs, in agreement with a modified Bragg's law expression. Calculated photonic band structures for the photocatalysts revealed a PBG along the $\Gamma \rightarrow L$ direction at $a/\lambda \sim 0.74$, in agreement with the experimental optical data. By coupling the low frequency edge of the PBG along the [111] direction with the electronic absorption edge of anatase TiO₂, a two-fold enhancement in the rate of gas phase ethanol photo-oxidation in air was achieved. This enhancement appears to be associated with a 'slow photon' effect that acts to both enhance TiO₂ absorption and inhibit spontaneous emission (i.e. suppress electron-hole pair recombination).

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1. Introduction

Titania (TiO₂) photocatalysts attract widespread research interest owing to their potential in solar energy capture and pollution abatement. The photocatalytic activity of TiO₂ is highly dependent on charge carrier concentrations generated under UV excitation ($E > E_g$, where E_g is the TiO₂ electronic band gap). A prudent approach for increasing the performance of semiconductor photocatalysts is to suppress electron-hole recombination, with numerous approaches such as surface functionalization of TiO₂ with electron or hole acceptors commonly being used to facilitate charge separation [1–6]. Photonic band gap (PBG) engineering is an alternative and far more challenging strategy for suppressing electron-hole pair recombination in TiO₂ and enhancing photoreaction rates [7–9]. Whilst the ability of photonic crystal engineering to enhance the performance of TiO₂ photocatalysts has long been recognized [8,9], experimental challenges associated with

the fabrication TiO₂ photonic crystals with appropriate optical properties needed to suppress electron-hole pair recombination in TiO₂ and achieve the so-called "slow photon" photocatalytic enhancement has handicapped progress in this field [7]. Reliable synthetic approaches towards TiO₂ photonic crystals with PBGs at near UV wavelengths where both TiO₂ absorption and electron-hole pair recombination occur are needed.

Titania inverse opal (IO) photonic crystals comprise a face-centred cubic (*fcc*) array of air spheres in a TiO₂ matrix, and are readily synthesized by the colloidal crystal template approach. The approach involves the self-assembly of monodisperse polymer colloids on a face-centred cubic lattice (to form a synthetic opal), followed by infiltration of the colloidal crystal with TiO₂ via sol–gel or atomic layer deposition (ALD) methods. Calcination of the resulting composite crystallizes the TiO₂ network and selectively removes the polymer template, yielding a 3-dimensionally ordered macroporous (3DOM) TiO₂ IO photonic crystal. The TiO₂ IO photonic crystals possess periodically modulated refractive indices along different directions in their *fcc* structure. Periodicity gives rise to PBGs, narrow frequency bands for which light propagation in the structure is forbidden (PBGs are the optical equivalent of electronic

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band gaps) [8,10,11]. The optical properties of polymer colloidal crystals and their TiO₂ IO replicas are adequately described by the modified Bragg's law expression below [12], which considers both refraction and diffraction of light in the photonic crystals:

$$\lambda_{\max} = 2d_{hkl} \sqrt{n_{\text{avg}}^2 - \sin^2 \theta} \quad (1)$$

where λ_{\max} (nm) is the PBG position for 1st order Bragg diffraction on a particular set of *fcc* planes, d_{hkl} (in nm) is the inter-planar spacing, n_{avg} is the average refractive index of the photonic crystal and θ is the incident angle of incident light with respect to the surface normal. TiO₂ IOs typically have solid volume fractions in the range 10–20%, and average refractive indices in air of 1.1–1.25.

The ability of photonic crystals to inhibit spontaneous emission in semiconductor photocatalysts was first proposed by Yablono-vitch et al. [10,13]. Fig. 1 (left), modified from Ref. [10], shows the semiconductor electronic band gap, E_g (the electron wavevector (\vec{k}) is $\vec{k}/1000$ as atomic spacings are ~ 1000 times smaller than optical wavelengths). The middle section of the diagram shows a portion of an optical dispersion relation with the second and third photonic bands (solid lines) converging at the (1 1 1) plane (i.e. at the L-point of the Brillouin zone, BZ). The group velocity (V_g) of light in a photonic crystal depends on the slope of the bands in the band structure (Fig. 1, plot of ω vs. \vec{k}), thus $V_g = \partial\omega/\partial \vec{k}$. At the confines of the PBG where the slope approaches zero (circles in Fig. 1), the V_g is strongly reduced, a phenomenon referred to as 'slow photons' [14,15]. The right hand part of Fig. 1 shows a TiO₂ IO reflectance spectrum, showing the PBG along the [1 1 1] or $\Gamma \rightarrow L$ direction described by Eq. (1). For anatase TiO₂ ($E_g = 3.2$ eV), electron-hole pair recombination is accompanied by the emission of a photon equal to E_g . If the red-edge of the TiO₂ IO PBG (the edge at which the electric field of the incident light is localized on the dielectric) is coincident with electronic band gap energy (3.2 eV or ~ 388 nm) of TiO₂, charge carrier recombination via photon emission should be effectively suppressed as the optical den-

sity of states is zero [10]. Thus, slow photon enhancement should be realized when the PBG reflectance maximum for a TiO₂ IO along the [1 1 1] direction is approximately 340–350 nm in a particular reaction medium.

A reduced group velocity of electromagnetic radiation at the red edge of the PBG has been shown to enhance the absorbance of dyes adsorbed on TiO₂ IO [16] and thereby enhance dye sensitized solar cell (DSSC) performance. In addition to suppressing electron-hole pair recombination, the low V_g at the red edge of PBG has been proposed to enhance momentum transfer between incoming photons and the semiconductor, thus enhancing absorption and increasing charge carrier formation [7,14]. Chen et al. observed a twofold enhancement in the photo-decomposition rate of methylene blue when the low energy edge of the PBG in an anatase TiO₂ IO aligned with the electronic absorption edge of anatase (~ 3.2 eV) [14]. Waterhouse et al. found that tuning the PBG along the [1 1 1] direction in Pd-Au/TiO₂ IO photocatalysts to the E_g of anatase resulted in a considerable enhancement of the photocatalytic water splitting to H₂ under both direct sunlight and UV irradiation [9]. A similar effect was seen by Sordello et al. in photocatalytic H₂ production over Pt-loaded TiO₂ inverse opals in powder form [17]. A distinct increase in activity was seen in an IO with a PBG at 365 nm compared to samples where the PBG red edge did not coincide with the TiO₂ electronic band gap. The increase in activity was attributed to the improved capture of light by the macroporous inverse opals structure. Coupling light trapping by SnO₂ inverse opal photonic crystals with absorption of evanescent waves by thin nc-TiO₂ layers resulted in an increased photocatalytic reaction rate for Rhodamine B decomposition [18]. Here the SnO₂/TiO₂ heterojunction played a strong role in enhancing absorption of photons by TiO₂. Similarly, an inverse opal CeO₂/TiO₂ heterostructure showed excellent photocatalytic activity for CO₂ reduction under simulated solar irradiation [19]. A combination of synergistic heterojunction charge transfer effects and the strong ability of the inverse opal structure to harvest light were proposed as reasons for the high

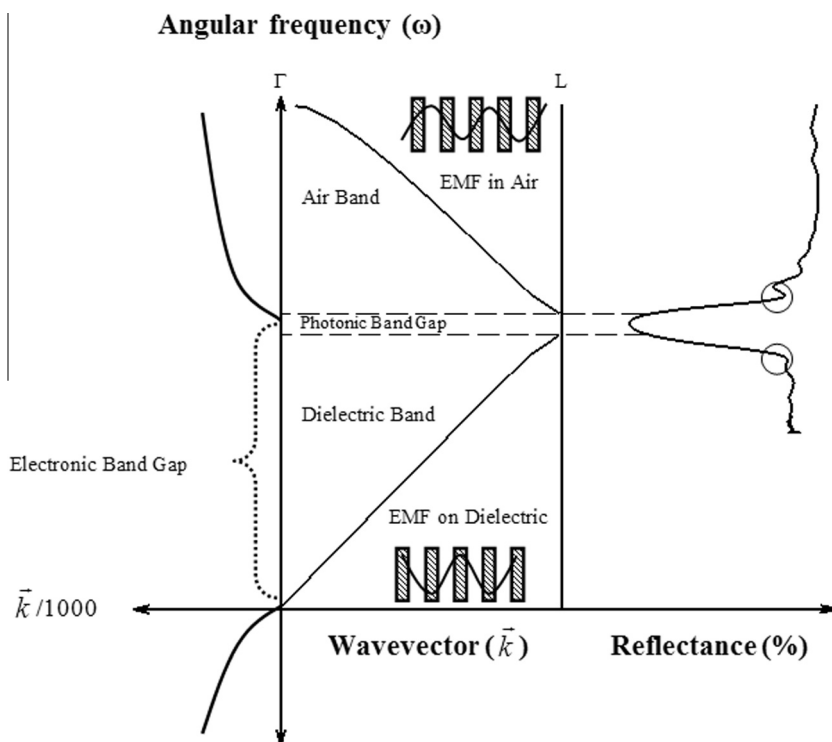


Fig. 1. Inhibition of spontaneous emission in a TiO₂ inverse opal photonic crystal (EMF = 'electromagnetic field'). This figure was adapted from the work of Yablono-vitch et al. [10].

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