Semiconducting Metal Oxide Photonic Crystal Plasmonic Photocatalysts

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Plasmonic photocatalysis has facilitated rapid progress in enhancing photocatalytic efficiency under visible light irradiation. Poor visible-light-responsive photocatalytic materials and low photocatalytic efficiency remain major challenges. Plasmonic metal–semiconductor heterostructures where both the metal and semiconductor are photosensitive are promising for light harvesting catalysis, as both components can absorb solar light. Efficiency of photon capture can be further improved by structuring the catalyst as a photonic crystal. Here, the synthesis of photonic crystal plasmonic photocatalyst materials using Au nanoparticle-functionalized inverse opal (IO) photonic crystals is reported. A catalyst prepared using a visible-light-responsive semiconductor (V$_2$O$_5$) displayed over an order of magnitude increase in reaction rate under green light excitation ($\lambda = 532$ nm) compared to no illumination. The superior performance of Au-V$_2$O$_5$ IO is attributed to spectral overlap of the electronic bandgap, localized surface plasmon resonance, and incident light source. For the Au-TiO$_2$ catalyst, despite coupling of the LSPR and excitation source at $\lambda = 532$ nm, this is not as effective in enhancing photocatalytic activity compared to carrying out the reaction under broadband visible light, which is attributed to improved photon adsorption in the visible by the presence of a photonic bandgap, and exploiting slow light in the photonic crystal to enhance photon absorption to create this synergistic type of photocatalyst.

1. Introduction

Plasmonic nanoparticles strongly absorb visible light due to their localized surface plasmon resonance (LSPR) resulting in photo generated electrons and holes which can be utilized for enhanced photocatalysts. Direct plasmonic photocatalysis describes chemical transformations which occur at the surface of the plasmonic NP under the excitation of the LSPR.$^\text{[1]}$ A variety of plasmon-induced chemical reactions have been reported such as oxidation,$^\text{[2]}$ coupling reactions,$^\text{[3]}$ H$_2$$^\text{[4]}$ and S–S$^\text{[5]}$ bond dissociation, and others which have been subject to extensive reviews.$^\text{[6]}$ Another general class of plasmon-enhanced photocatalysts are based on metal–semiconductor heterostructures which have shown promise for photocatalytic conversion of light energy.$^\text{[7–9]}$ Incorporating plasmonic NPs into wide bandgap semiconductors, such as Au-TiO$_2$ systems, extends light absorption of the semiconductor into the visible range as plasmon-generated hot electrons can transfer to the semiconductor thereby prolonging the lifetime of charge carriers.$^\text{[7,10]}$ Electrons transferred to the semiconductor drive reduction processes and holes left in the metal NP can induce oxidative transformations enabling applications for water splitting,$^\text{[11]}$ CO$_2$ reduction,$^\text{[12]}$ pollutant degradation,$^\text{[13]}$ aerobic oxidation,$^\text{[14]}$ and selective hydrogenation of cinnamaldehyde,$^\text{[15]}$ as an example. Combining plasmonic NPs with narrow bandgap (vis-NIR) semiconductors has been less studied in comparison, but these systems enable both the metal and the semiconductor support to be sensitized by visible light. When the plasmon resonance of the NPs overlaps with the electronic absorption of the semiconductor, incident light simultaneously excites the LSPR in the NPs and generates electron-hole pairs in the semiconductor giving rise to strong local field effects.$^\text{[16]}$ Charge transfer can occur from metal to semiconductor or vice-verse depending...
on the nature of the band alignment. Super-resolution mapping of photogenerated electrons in Au-tipped CdS heterostructures verified the existence of two fundamentally distinct charge separation mechanisms in systems when both the metal and semiconductor are excited by the incident light source. Therefore, through selection of the appropriate metal NP and semiconductor support, such heterostructures potentially enable the flow of electrons to be for optimized for a particular reaction under visible light.

In addition to a well-designed energy band structure to modulate charge-carrier generation and migration, the overall catalyst architecture plays an important role in the photocatalytic enhancement observed. In particular, the semiconductor superstructure influences the migration of excited electrons and enable longer charge carrier lifetimes. At the semiconductor-solution interface, small dimensions that approach the depletion layer width of the semiconductor can deplete the material of majority carriers, but physically structuring the semiconductor to maximize ionic and electronic mobility can be very useful. The use of photonic crystals as catalyst support architectures has generated considerable interest for light harvesting catalytic applications as their unique optical and structural features to be exploited for enhanced performance.

Photonic crystals influence the propagation of light by their periodic variation in dielectric contrast. One very useful property of photonic crystals is the phenomenon of slow group velocity photons, or “slow” light. At energies close to the photonic bandgap, the group velocity of light is retarded, giving rise to the slow photon effect which can increase the degree of light absorption and can be exploited for photocatalytic applications. Furthermore, trapping of light at standard group velocities by a photonic crystal that acts as a dielectric mirror may also contribute to enhanced photocatalysis. By combining plasmonic and photonic nanostructures, it is possible to tune the electronic absorption of the semiconductor bandgap with the LSPR of the metal NP and a photonic bandgap of the semiconductor support. This synergy can be used to maximize the photon-to-electron efficiency for electron injection into the oxide conduction band or the metal NP surface, depending on the barrier height and alignment. Zhang et al. assembled Au NPs on TiO$_2$ nanotube arrays where the LSPR wavelength matched the photonic bandgap of the TiO$_2$ support, increasing hot electron injection and improved performance in photoelectrochemical (PEC) water splitting. Other nanostructures effectively integrating the photonic bandgap with the LSPR include Au-TiO$_2$ bilayer nanorod-photonic crystal for water PEC systems, thin shell Au/TiO$_2$ hollow nanospheres for decomposition of isopropanol to CO$_2$ and Au-ZnO photonic crystals for degradation of rhodamine blue. The plasmonic effect of Au NPs deposited on visible light active semiconductor bismuth vanadate (BiVO$_4$) and CdS-Au-WO$_3$ was significantly amplified due to strong coupling with the photonic Bragg resonance, resulting in high performance catalysts for photocatalytic water splitting. In addition to the unique optical properties of photonic crystals, the interconnected porous networks enable favorable mass transport of reactants in solutions. The catalyst architecture also remains electrically interconnected as a porous monolithic support which can improve charge carrier lifetime compared to assemblies or powders.

In this work, we developed a metal-semiconductor photocatalyst that uses a synergy of LSPR at the Au NP surface, electronic absorption of the semiconductor support, and slow photon effects near a pseudophotonic bandgap of an inverse opal (IO) photonic crystal to enhance light absorption (white light or monochromatic) for plasmonically enhanced photocatalysis. Plasmonic photocatalysts are prepared by depositing monodisperse Au NPs on a photonic crystal V$_2$O$_5$ support with an IO structure. V$_2$O$_5$ is a visible light responsive, photocatalyst with an optical bandgap of $E_g \approx 2.3$ eV. V$_2$O$_5$-graphene nanostructures showed strong degradation efficiency of dyes with direct sunlight irradiation and coupling V$_2$O$_5$ with TiO$_2$ or SnO$_2$ has been shown to improve photocatalytic efficiency. Catalytic performance is compared with Au-TiO$_2$ catalysts by depositing Au NPs onto TiO$_2$ IOs with an bandgap of $\approx 3.2$ eV (for anatase form). The catalytic activity for hydrogenation of nitrophenol is investigated under different illumination conditions using broadband UV–vis light, monochromatic green light ($\lambda = 532$ nm) and under no illumination. The highest catalytic enhancement was achieved when Au NPs were deposited on a visible light responsive semiconductor, V$_2$O$_5$ IO catalyst under green light excitation due to spectral overlap of the electronic bandgap, LSPR and excitation source. We further demonstrate a significant influence of the semiconductor superstructure by comparing nonporous supports with photonic crystal supports which enable photonic bandgap (PBG) and slow light effects for further photocatalytic enhancement resulting in a doubling of the reaction rates for both V$_2$O$_5$ and TiO$_2$ IO structures compared to nonporous catalysts.

2. Results and Discussion

2.1. Plasmonic Photonic Crystal Photocatalysts

Figure 1 summarizes four characteristics we exploit to maximize photocatalytic activity: Hot electron effects at the surface of Au NPs under white and green light illumination, the photonic bandgap of the oxides to maximize absorption, slower group velocity for photons in the energy range of interest, and control over electron transfer from Schottky barriers between the Au NP and each oxide. Plasmonic photonic crystal photocatalysts were prepared using a stepwise approach by combining inverse opal (IO) thin film coatings with monodisperse colloidal Au NPs. First, IO thin films of V$_2$O$_5$ and TiO$_2$ were prepared on ITO substrates by infiltration of liquid precursors into polystyrene templates. The resulting IO photocatalytic structures were surface functionalized with Au NPs. Figure 2a,b shows scanning electron microscopy (SEM) and transmission electron microscopy (TEM) analysis of the V$_2$O$_5$ IO, with the internal walls of the IO framework consisting of a layered structure, typical of orthorhombic V$_2$O$_5$ which is a vdW layered material. Further details can be seen in Figures S1 and S2 (Supporting Information). X-ray diffraction (XRD) of the V$_2$O$_5$ and TiO$_2$ IOs (Figure S3, Supporting Information) confirms crystalline orthorhombic V$_2$O$_5$ and anatase TiO$_2$ of the materials in IO form. In comparison, the morphologies of IO TiO$_2$ IOs is comprised of interconnected TiO$_2$ NPs, as shown in Figure 2c,d...
Figure 1. Representation of semiconductor photonic crystal plasmonic photocatalyst design and synergy. Inverse opal photonic crystals functionalized with Au NPs photocatalytically reduce nitrophenol under green (532 nm) laser light or broadband white light. Both TiO$_2$ and V$_2$O$_5$ are examined, with bandgaps in the UV ($\approx$ 3.2 eV) and visible regions ($\approx$ 2.3 eV), respectively. The system involves surface plasmon-mediated hot electrons at the Au surface, band-edge absorption from the semiconducting metal oxide, Schottky barrier from semiconductor-metal interface, and pseudophotonic bandgap (including slow photon effects) from the inverse opal, to tune light absorption and electron transfer during photocatalysis.

Figure 2. a) SEM and b) TEM images of V$_2$O$_5$ inverse opals and the vdW layered internal structure of the vanadate IO walls, and the infilling of the tetrahedral and octahedral voids of the parent opal template. c) SEM and d) TEM images of the TiO$_2$ IO material. The inset shows HRTEM images of the Au NP-TiO$_2$ IO interface after NP functionalization. e) TEM image of synthesized Au NPs. f) V$_2$O$_5$ IO after Au NP immobilization. g) EDX line scan of V$_2$O$_5$ and h) TiO$_2$ IO photocatalysts decorated with immobilized Au NPs.
with internal pore diameters that are \(\approx 460\) nm in diameter.\(^{[33]}\) Similar pore dimensions that are also found on the \(\text{V}_2\text{O}_5\) IO structures (Figure S4, Supporting Information). A colloidal solution of monodisperse Au NPs with a mean diameter of 4.5 nm, shown in Figure 2e, was immobilized onto the IO supports giving well-dispersed Au NPs across the IO as shown in Figure 2f. Using Au NPs dispersed in low dielectric constant solvent such as hexane, coupled with a large PS template (500 nm) allows the NP solution to percolate through the IO support.\(^{[34]}\) SEM image and energy dispersive X-ray (EDX) analysis shown in Figure 2g,h and in Figure S5 (Supporting Information), confirms Au decoration of the \(\text{V}_2\text{O}_5\) and \(\text{TiO}_2\) IO supports. Nonporous Au-NP decorated thin films of each oxide were also prepared to determine the influence of the IO structure on catalytic performance. The deposition of 15 nm citrate stabilized Au NPs onto the IO supports was also investigated. TEM analysis showed that while some regions displayed good NP dispersion, the use of larger NPs in aqueous media resulted in considerable NP agglomeration at the surface of the IO rather than percolating through the porous structure (Figure S6, Supporting Information).

Figure 3a,b shows the \(\text{V}_2\text{p}\) and \(\text{O}1\text{s}\) core level spectra of the IO supports, respectively. The \(\text{V}_2\text{p}\) spectrum confirms the presence of \(\text{V}^{5+}\) oxidation state with peaks for the \(\text{V}_2\text{p}\) doublet at binding energies (B. E.) of 517.7 and 525.2 eV, assigned to \(\text{V}^{5+}\) 2p\(_{3/2}\) and \(\text{V}^{5+}\) 2p\(_{1/2}\), respectively. The \(\text{O}\) 1s signal in the same spectrum shows photoemission at 530 and 532.2 eV, attributed to the surface lattice oxygen and adsorbed oxygen species, respectively.\(^{[35]}\) The \(\text{Ti}2\text{p}\) spectrum shows the doublet at 464.8 and 459.2 eV assigned to \(\text{Ti}2\text{p}_{3/2}\) and \(\text{Ti}2\text{p}_{1/2}\) respectively. From the Au 4f spectra is shown in Figure 3c the B. E. of the unsupported Au NPs at 83.6 eV is positively shifted to 84.4 eV when immobilized on \(\text{V}_2\text{O}_5\) and negatively shifted to a lower B. E. of 83.4 eV when immobilized on \(\text{TiO}_2\). A B. E. difference of +1.2 eV between the two support materials is indicative of Au being more electron deficient when deposited on \(\text{V}_2\text{O}_5\) compared to \(\text{TiO}_2\). This charge transfer can be rationalized by comparison of the relative work functions (WFs) of the two semiconductor supports.\(^{[36]}\)

To tune the synergy of material and optical properties, we first characterized the spectral overlap of the LSPR for Au NPs and the photonic bandgap and band-edge absorption for the \(\text{V}_2\text{O}_5\) and \(\text{TiO}_2\) IOs. The optical bandgap energies, IO photonic bandgap ranges and absorption resonance of the Au NPs were determined for the \(\text{V}_2\text{O}_5\) and \(\text{TiO}_2\) IOs with and without Au NP functionalization. Figure 4a,b shows the absorption spectra for Au NPs in solution, confirming an LSPR of \(\approx 530\) nm. Transmission spectra of the IOs at normal incidence show the location of the band-edge, and the stop band associated with a pseudophotonic bandgap, effectively extending the energy window for photon absorption for white light. Optical bandgaps were estimated from UV–vis absorption spectra and analyzed in the framework of the Tauc model. Figure 4c,d shows the plots of \((\alpha h\nu)^2\) versus \(h\nu\) where \(\alpha\) is the absorption coefficient near the absorption edge, \(h\) is Planck’s constant and \(\nu\) is the photon frequency. The extrapolated bandgap values were 2.3 eV for \(\text{V}_2\text{O}_5\) and 3.2 eV for \(\text{TiO}_2\), in good agreement with literature values.\(^{[37]}\) In the case of \(\text{TiO}_2\) with a bandgap in the UV, the Au decorated \(\text{TiO}_2\) IO absorption profile changes to show an sub-bandgap Urbach, further indicating light absorption extending...
into the visible region associated with the surface plasmon absorption from the Au NPs. Visible light adsorption is also further enhanced by the presence of the PBG associated with the IO structure (Figure 4a). The valence band position was evaluated from photoelectron valance band (VB) spectra of the catalysts before and after Au NP deposition. The VB density of states of bare V$_2$O$_5$ (Figure 4e) shows the band edge located at 2.9 eV and after Au deposition, the main absorption on-set in the VB spectrum shifts to 2.0 eV. The VB density of states of bare TiO$_2$ (Figure 4f) shows the band edge is 2.7 eV and after Au deposition, the spectrum is blue shifted to $\approx$2 eV.

### 2.2. Photocatalytic Enhancement from Synergy of LSPR, PBG, and Bandgap Absorption

Electron transfer of plasmonic NPs coupled with high bandgap semiconductors, such as Au-TiO$_2$ systems, is generally attributed...
to plasmonic sensitization.[38] A Schottky barrier, \( \phi_B = \phi_M - \chi \), is formed at the interface where \( \phi_M \) is the workfunction of Au and \( \chi \) is the oxide semiconductor electron affinity. Energies for hot electrons generated from excitation of the LSPR typically range from 1 to 4 eV, can then transfer into the TiO\(_2\) conduction band (CB) or the lowest unoccupied molecular orbitals of molecular adsorbates[39] as illustrated in Figure 5. The Schottky barrier height estimated using values of \( \phi_M = 5.1 \text{ eV} \) for Au, \( \chi_{\text{TiO}_2} = 4.0 \text{ eV} \) and \( \chi_{\text{V}_2\text{O}_5} = 6.3 \text{ eV} \,[40] \) correspond to 1.1 and –1.2 eV, respectively, thus favoring electron transfer to the Au NP from the \( \text{V}_2\text{O}_5\) CB and vice versa for TiO\(_2\). In the case of \( \text{V}_2\text{O}_5\), which is a visible light responsive semiconductor, light simultaneously excites the LSPR at the NP and electron/hole pair generation in the \( \text{V}_2\text{O}_5\). The energy level of the \( \text{V}_2\text{O}_5\) CB is higher than the Fermi level of the Au NPs and so excited CB electrons generated in \( \text{V}_2\text{O}_5\) should favor transfer to the Au NPs, as shown in Figure 5. Furthermore, the LSPR is resonant with the \( \text{V}_2\text{O}_5\) band edge which should further contribute to enhancing photocatalytic performance.

To further examine the nature of the photocurrent generation and electron transfer in Au NP-functionalized IOs, electrical transport measurements (in the dark and under illumination) were conducted. Figure 5d–f shows two terminal \( I-V \) curves for Au-\( \text{V}_2\text{O}_5\) and Au-TiO\(_2\) IOs under white light, excitation at \( \lambda = 532 \text{ nm} \), and in the dark. The Au-NP functionalized IO structures display typical behavior consistent with Schottky barriers to the n-type oxide from the In-Ga eutectic contacts. The Au-\( \text{V}_2\text{O}_5\) IO showed negligible photocurrent response using either light source as shown in Figure 5d. With a bandgap of 2.3 eV, \( \text{V}_2\text{O}_5\) would be expected to exhibit some photoresponse from both green and white light illumination in the form of a weak Schottky photodiode. This observation is attributed to extraction of electrons to an outer circuit to register as photocurrent is limited by direct and efficient electron transfer from the \( \text{V}_2\text{O}_5\) CB to the Au NPs in this case. By contrast, the photocurrents of the Au-TiO\(_2\) IO improved upon illumination with a halogen UV–vis light source and under \( \lambda = 532 \text{ nm} \) excitation, as shown in Figure 5e,f. In these cases, green light excites the Au NP LSPR which then, as illustrated in Figure 5b,c, transfers to the TiO\(_2\) CB, giving the observed photoresponse. Increased photocurrent is also observed under broadband visible light attributed both excitation of the LSPR and to VB-CB transitions in TiO\(_2\) from the UV-portion of the white light source exciting the bandgap (3.2 eV). Efficient electronic coupling and fast electron transfer between Au NPs and TiO\(_2\) supports has been confirmed by femtosecond transient absorption spectroscopy with an infrared probe.[41]

2.3. Quantifying the Enhancement from Photonic Crystal Plasmonic Photocatalysts

Testing the synergy between LSPR, band-edge electronic absorption, and maximizing optical path length and absorption using a plasmonic-photonic crystal architecture was done by exploring catalytic reduction of 4-nitrophenol (4-NP) by NaBH\(_4\), which is often used as a model reaction to evaluate the behavior of metal NPs.[42] The reaction proceeds via the intermediate 4-hydroxylaminophenol, and requires that both reactants (4-NP and BH\(_4^{-}\)) must

![Figure 5. Band structure comparing Au NP supported on a) \( \text{V}_2\text{O}_5\) under white light and \( \lambda = 532 \text{ nm} \), b) TiO\(_2\) under \( \lambda = 532 \text{ nm} \) irradiation, and c) TiO\(_2\) under white light illumination. SP represents surface plasmons, CB is conduction band, and VB is valence band. \( I-V \) curves acquired at room temperature of Au NP-functionalized d) \( \text{V}_2\text{O}_5\) and e) TiO\(_2\) materials under halogen white light and f) a separate Au-TiO\(_2\) IO excited by \( \lambda = 532 \text{ nm} \) photons.](image-url)
first absorb on the metal surface. The apparent rate constant $k_{app}$ was estimated for the Au-decorated TiO$_2$ and V$_2$O$_5$ IO catalysts from in situ UV–vis spectroscopy which monitored the decrease in the characteristic absorption peak of 4-NP at $\lambda = 400$ nm. Figure S7 (Supporting Information) shows the UV–vis spectra of the IO catalysts under no illumination, a broadband white light halogen lamp and under green laser excitation at $\lambda = 532$ nm.

Figure 6 compares the catalytic and photocatalytic activity of the IO substrates determined from the in situ UV–vis spectra under the different illumination conditions (see the Experimental Section for details). The $k_{app}$ for Au-V$_2$O$_5$ IO without any illumination was $1.26 \times 10^{-3}$ s$^{-1}$, and this rate almost doubled to $2.2 \times 10^{-3}$ s$^{-1}$ under visible light irradiation. On excitation with green light at $\lambda = 532$ nm, the rate increased by an order of magnitude with $k_{app} = 1.16 \times 10^{-2}$ s$^{-1}$. The large $k_{app}$ when the excitation wavelength is coincident with the LSPR is indicative of plasmonic photocatalysis being responsible for higher reaction rate under illumination. Figure 6b shows the catalytic performance of the Au-TiO$_2$ IO catalyst, which also displayed photocatalytic enhancement but to a lesser degree compared to Au-V$_2$O$_5$. Under no illumination, the $k_{app}$ estimated for the Au-TiO$_2$ IO was $8.25 \times 10^{-4}$ s$^{-1}$, ~60% lower than that of the V$_2$O$_5$ catalyst, demonstrating the Au-V$_2$O$_5$ system to be a general superior catalyst for this reaction. A longer induction period of ~60 s was observed for the reactions catalyzed by the Au-TiO$_2$ IOs. Induction periods are sometimes observed for this reaction and have been associated with surface restructuring of the NP before the adsorption of the reagents.[43] As the same colloidal Au NPs were used for both TiO$_2$ and V$_2$O$_5$, charge transfer at the metal–semiconductor interface, as identified by the shifts in the Au 4f core-level B.E., may contribute to the longer induction period observed for TiO$_2$.

Photocatalytic enhancement for the Au-TiO$_2$ IO was highest under UV–vis light irradiation, with the reaction rate increasing by ~70% ($k_{app} = 1.37 \times 10^{-3}$ s$^{-1}$). Interestingly, despite the green light excitation being coincident with the Au SPR, the photocatalytic activity of the Au-TiO$_2$ IO under $\lambda = 532$ nm ($k_{app} = 1.19 \times 10^{-3}$ s$^{-1}$) was lower than under halogen light irradiation. As shown in the absorbance spectra (Figure 3a) while the LSPR is not resonant with the TiO$_2$ band edge, the Au-TiO$_2$ IO catalyst does show strong visible light absorption associated with the PBG, thereby leading to improved catalytic performance under visible light. The UV component of the halogen light source which can excite the TiO$_2$ bandgap may also play a role in the enhanced activity.

To further study the slow photon effect in these photonic crystal photocatalyst systems, the nature of slow group velocity photons in the TiO$_2$ and V$_2$O$_5$ IOs immersed in the solution ($n_{sol} = 1.45$) was evaluated. The IOs are designed such that the optical path length increase from slow photons at the higher energy edge of the photonic bandgap, where the electric field is localized within the higher index material (metal oxide).[44] Using the optical transmission data acquired at normal incidence (see Figure S8, Supporting Information), we calculated the respective group index $n_g = c/v_g = (4 \pi n_{sol}^2)/(\omega_0^2)$ for both IOs, shown in Figure 7. More information on the finite difference time domain models can be found in the Supporting Information and in Figures S9 and S10 (Supporting Information). Using a Drude approximation, $n_{eff} = 1.82$ and 1.56 for TiO$_2$ and V$_2$O$_5$ IOs, leading to reduced group indices shown in Figure 7a, b, which illustrates that photon absorption across the visible range is enhanced by the slow photon effect in both TiO$_2$ and V$_2$O$_5$ IOs catalysts. For V$_2$O$_5$, the optical path length $L = n_{eff} \cdot s$ where $s$ is the geometrical length, is a factor of 1.2 greater for V$_2$O$_5$ IO at $\lambda = 532$ nm.

Notably, over the entire spectral range examined in Figure 7, TiO$_2$ has a longer effective optical path length (higher group index from slow light) at all frequencies under transverse magnetic (TM) or transverse electric (TE) polarizations. This is relevant for enhanced photon absorption and photocatalysis under white light illumination, which correlates well to the superior activity observed under broadband visible light. For example, the maximum effective increase in group index for TiO$_2$ (Figure 7a) at $\lambda = 558$ nm is a factor $1.52 \times$ greater than for the V$_2$O$_5$ IO. The maximum enhancement effect ($1.75 \times$) is found at $\lambda = 580$ nm.

The behavior of the metal–semiconductor hetero-structured catalysts under broadband white light is of particular interest for harvesting solar energy for sustainable catalysis and so the photocatalytic rate behavior was evaluated further. To study the inherent structural features of the IO...
architecture, and synergy between the oxide bandgap, PBG and slow light effect as demonstrated in Figure 7, nonporous catalysts of TiO$_2$ and V$_2$O$_5$ were prepared using the same procedure as the IOs but in the absence of the IO structure-defining polystyrene template. XRD patterns (Figure S1, Supporting Information) and atomic force microscopy (AFM) images of the nonporous catalytic thin films are shown in Figure S11 (Supporting Information), confirming the same

![Diagram](image)

**Figure 7.** Computed variation of the group index $n_g$ for reaction solution-infiltrated TiO$_2$ and V$_2$O$_5$ IO photonic crystal photocatalysts in a) TM and b) TE polarizations. The regions for higher group index (slow photon group velocity $n_g = c/\nu_g > n_{eff}$) are shaded in a). The effective index $n_{eff}$ for the solution-filled IO medium for each case are shown by the dashed horizontal lines.

![Graphs](image)

**Figure 8.** Reaction profiles for plasmonic photocatalytic 4-nitrophenol reduction using IO and nonporous thin films a) V$_2$O$_5$ and b) TiO$_2$ catalysts in the dark and under visible light and monochromatic (green) irradiation. c,d) Bar chart comparing rate contribution under different illumination for IO and nonporous V$_2$O$_5$ and TiO$_2$ catalysts.
stoichiometric crystalline phase of $V_2O_5$ and TiO$_2$ in both cases. Figure 8a,b compares the reaction rate profiles of the Au-$V_2O_5$ and Au-TiO$_2$ IO supports, and Au NP-decorated nonporous supports, respectively. Band alignment, LSPR and band-edge absorption are nominally similar in both sets of catalyst systems, with exception of the IO structure. Under visible light the $V_2O_5$ catalyst with an IO structure displayed a doubling of the rate compared to the nonporous $V_2O_5$ catalysts. Similar enhancements were observed for the Au-TiO$_2$ IO catalysts compared to the nonporous TiO$_2$ catalyst, indicating the support architecture plays a key role in the photocatalytic enhancement. This rate enhancement can be attributed to the slow photon effect and the ordered IO superstructures which increase charge separation, prolonging the lifetime of charge chargers.[10] The reaction data in Figure 8a,b further demonstrates that both $V_2O_5$ and TiO$_2$ catalysts having an IO architecture display enhanced performance even under no illumination, which originates from the ordered macroporous IO structure which is known to be beneficial for liquid and vapor phase reactions due to efficient mass transport and wetting of surfaces to allow infiltration of reaction species.[45]

The bar chart in Figure 8c,d compares reaction performance of catalysts having an IO and nonporous structure under different illumination conditions (broadband vs monochromatic). Within these Au–semiconductor catalysts the catalytic enhancement can originate from a synergy of effects (cf. Figure 1) associated with i) the LSPR of Au NPs at 520 nm, ii) Schottky barrier-mediated charge-transfer at Au–semiconductor interface, and iii) the role of the IO superstructure and PBG compared to nonporous supports. Catalytic enhancement associated with coupling these effects is clearly demonstrated for the Au-$V_2O_5$ IO under excitation at $\lambda = 532$ nm, when the $V_2O_5$ electronic bandgap (2.3 eV) overlaps with the Au NP LSPR ($\approx 530$ nm) in the same energy region as the lower photon group velocity of the photonic bandgap (slow light effects), resulting in an order of magnitude rate increase. The rate enhancement obtainable in the Au-$V_2O_5$ catalyst under UV–vis light was lower by a factor of five without these synergistic effects. Specifically engineering the energy range to use LSPR, oxide bandgap and PBG (including light trapping) using slow photon effects, significantly enhances plasmonic photocatalysis from Au-$V_2O_5$ IO where charge transfer is optimized to the catalyzing Au NP interface.

In the case of the Au-TiO$_2$ catalyst, plasmonic enhancement is mainly limited to plasmonic sensitization due to the wider bandgap of TiO$_2$ (3.2 eV). The relative work-functions and associated band bending promote electron injection into the TiO$_2$ CB, the opposite charge transfer observed for the Au-$V_2O_5$ catalyst, as illustrated in Figure 5. For the Au-TiO$_2$ catalyst despite the excitation wavelength at $\lambda = 532$ nm being near-resonant with the LSPR, a greater photocatalytic enhancement is observed under broadband halogen light, attributed with the presence of the PBG enabling visible light adsorption (Figure 3) and associated slow photon effects (Figure 7). Furthermore, the UV component of the halogen light can generate electron-hole pairs in addition to hot electrons from the Au into the CB which may also contribute to the enhanced photocatalytic activity observed. Although the exact mechanism of this catalytic behavior is unclear, several studies demonstrate the multifaceted nature with positive and negative effects arising from the LSPR in Au/TiO$_2$ structures under different illumination sources.[46]

3. Conclusions
Plasmon-enhanced photocatalysis holds significant promise for enhanced performance and controlling chemical reaction rates. Semiconductor photocatalysts with an inverse opal structure offers a large active surface area, electrically interconnected porous network which can be functionalized with plasmonic NPs to form plasmonic-photonic catalysts with broad visible absorption due to the presence of a PBG to further enhance the efficiency. The use of $V_2O_5$ as a visible light semiconductor catalyst allowed several synergistic effects including the LSPR, electronic bandgap, PBG and slow photon effects, resulting in superior performance to a conventional TiO$_2$ support for hydrogenation of 4-nitrophenol. Both $V_2O_5$ and TiO$_2$ IO catalysts have superior photocatalytic compared to nonporous catalysts due to integration of the Au LSPT and the PBG associated with the IO structure of the support. Overall, this strategy takes many of the chemical, material and photonic strategies used to control photon-to-electron conversion for photocatalysis in a synergistic way to improve visible light operation. The modularity of the synthesis approach facilitates rational design of efficient plasmonic photocatalysts as the nanoparticle and semiconductor components can be readily altered, enabling it to be extended to other metal–semiconductor composites for a variety of catalytic applications.

4. Experimental Section
All chemicals used unless otherwise stated were purchased from Sigma–Aldrich and used as received.

Au Nanoparticle Synthesis: Au NPs were prepared using a previously published method.[47] Briefly, HAuCl$_4$ (200 mg) were combined with oleylamine (OAm, 20 mL) and 20 mL of 1,2,3,4-tetrahydronaphthalene (20 mL) in a round bottom flask. t-Butylamine-borane complex (86 mg, 1 mmol) dissolved in of OAm (2 mL) and of oleylamine (OAm, 20 mL) and 20 mL of 1,2,3,4-tetrahydroindanaphthalene (2 mL) was quickly injected into the solution. The solution was stirred in air for 1 h. The particles were precipitated using ethanol and centrifugation at 8000 rpm for 20 min for three cycles before being dispersed in 20 mL of toluene.

Inverse Opal Synthesis and NP Immobilization: Synthesis of $V_2O_5$ and TiO$_2$ IO on fluorine-doped tin oxide (FTO) was carried out using a previously described procedure.[48] Briefly, Au NCs were formed by electrochemically depositing $\approx 500$ nm PS spheres on FTO-glass substrates, cleaned with acetone, IPA, and deionized water. A 50:1 ratio of IPA to vandadium triisopropoxide oxide (OV(OC(CH$_3$)$_3$)$_3$) was added to a 500:1 IPA-deionized water mixture and stirred until clear, forming a 1000:10:1 precursor solution. The precursor was then drop cast onto opal templates and annealed in an oven at 300 °C for 12 h to remove the template. TiO$_2$ IOs were synthesized by dissolving TiCl$_4$.2THF (334 mg) in IPA, forming a 0.1 w precursor solution. Samples were annealed at 450 °C for 1 h. $V_2O_5$ and TiO$_2$ nonporous thin films were formed by drop-casting the IPA-precursor solutions into cleaned FTO substrates to obtain a uniform thin film coating. $V_2O_5$ and TiO$_2$ samples were crystallized by annealing at 300 °C (12 h) and 450 °C (1 h), respectively. Au nanoparticles
immobilization was carried out by immersing the substrates in Au NP solution (1 mg mL⁻¹) overnight. The substrates were removed and left to dry. Substrates were rinsed with toluene to remove excess Au NPs and dried in air.

**Reaction Studies:** Catalytic reduction of 4-nitrophenol (TCI Chemicals) was investigated using in situ UV–vis spectroscopy. The UV–vis spectral analysis was carried out using a quartz tungsten-halogen lamp operating from 400 to 2200 nm from Thorlabs Inc., a UV–vis spectrometer (USB2000+ VIS-NIR-ES) with operational range 350–1000 nm from Ocean Optics Inc. A motorized rotation stage (ELLB, Thor Labs Inc.) was used to control the incidence angle in transmission measurements. Laser excitation at λ = 323 nm was supplied using a Laser Quantum GEM DPSS single transverse mode CW laser and focused using an objective lens. For catalysis studies, the reaction rate was determined by monitoring the decrease in absorption of 4-NP at λ = 400 nm. The apparent rate constant k_{app} was estimated from the slope of ln ([A]/[A₀]) vs time. In a typical reaction, 2 mL of deionized water, 0.25 mL of a 0.5 × 10⁻³ m solution of 4-nitrophenol and a stir bar were added to a polystyrene cuvette. The reaction was initiated by addition of 0.5 mL of freshly prepared 0.2 m NaBH₄ solution.

**Material Characterization:** SEM characterization was performed using a Hitachi S-4800 SEM cold field emission apparatus or an SU-70 SEM hot field emission apparatus. EDX spectroscopy was carried out using an Oxford X-Max 80 detector. TEM was carried out using a JEM2100-TEM. X-ray Photoelectron Spectroscopy (XPS) was acquired using a KRATOS AXIS 165 monochromatized X-ray photoelectron spectrometer equipped with an Al Kα (hv = 1486.6 eV) X-ray source. Spectra were collected at a take-off angle of 90° and all spectra were referenced to the C 1s peak at 284.6 eV. The spectra were fit to Voigt profiles using a Shirley background.

**Electrical Characterization:** Electrical conductivity measurements were performed using a Keithley Instruments 2612B Dual-Channel System Sourcimeter, with gold-coated probes and In-Ga eutectic as a contact.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or Supporting Information from the author.

**Conflict of Interest**

The authors declare no conflict of interest.

**Keywords**

catalyst, nitrophenol reduction, photocatalysis, photonic crystal, plasmonic nanoparticles

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