Composite Photocatalysts Containing BiVO4 for Degradation of Cationic Dyes

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Abstract
The creation of composite structures is a commonly employed approach towards enhanced photocatalytic performance, with one of the key rationales for doing this being to separate photoexcited charges, affording them longer lifetimes in which to react with adsorbed species. Here we examine three composite photocatalysts using either WO3, TiO2 or CeO2 with BiVO4 for the degradation of model dyes Methylene Blue and Rhodamine B. Each of these materials (WO3, TiO2 or CeO2) has a different band edge energy offset with respect to BiVO4, allowing for a systematic comparison of these different arrangements. It is seen that while these offsets can afford beneficial charge transfer (CT) processes, they can also result in the deactivation of certain reactions. We also observed the importance of localized dye concentrations, resulting from a strong affinity between it and the surface, in attaining high overall photocatalytic performance, a factor not often acknowledged. It is hoped in the future that these observations will assist in the judicious selection of semiconductors for use as composite photocatalysts.

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Composite Photocatalysts Containing BiVO\textsubscript{4} for Degradation of Cationic Dyes

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The creation of composite structures is a commonly employed approach towards enhanced photocatalytic performance, with one of the key rationales for doing this being to separate photoexcited charges, affording them longer lifetimes in which to react with adsorbed species. Here we examine three composite photocatalysts using either WO\textsubscript{3}, TiO\textsubscript{2} or CeO\textsubscript{2} with BiVO\textsubscript{4} for the degradation of model dyes Methylene Blue and Rhodamine B. Each of these materials (WO\textsubscript{3}, TiO\textsubscript{2} or CeO\textsubscript{2}) has a different band edge energy offset with respect to BiVO\textsubscript{4}, allowing for a systematic comparison of these different arrangements. It is seen that while these offsets can afford beneficial charge transfer (CT) processes, they can also result in the deactivation of certain reactions. We also observed the importance of localized dye concentrations, resulting from a strong affinity between it and the surface, in attaining high overall photocatalytic performance, a factor not often acknowledged. It is hoped in the future that these observations will assist in the judicious selection of semiconductors for use as composite photocatalysts.

Bismuth vanadate (BiVO\textsubscript{4}) has attracted much attention as a highly responsive, visible-light driven, photocatalyst due to its comparatively narrow band gap (E\textsubscript{g}) energy of 2.4 eV, (as compared to TiO\textsubscript{2}, which remains a benchmark, with an E\textsubscript{g} of 3.0–3.2 eV). BiVO\textsubscript{4} has been widely used in the photocatalytic degradation of organic compounds in waste water as well as for O\textsubscript{2} evolution under sunlight irradiation\textsuperscript{1–4}.

One of limitations of the photocatalytic efficiency in BiVO\textsubscript{4} is the recombination of photogenerated electrons and holes, with the free carrier life time reported to be about 40 ns by Abdi \textit{et al.}\textsuperscript{5}. In order to enhance these lifetimes, the creation of electronic barriers, facilitating spatial separation of the photogenerated electrons and holes, has been embraced by researchers as they can retard this recombination, providing more opportunities for free holes and electrons to participate in reduction and/or oxidation reactions, such as for the degradation of organic materials\textsuperscript{4,6}. Doping semiconductors, either with metal or non-metals, has also been demonstrated to be an effective method for enhancing photocatalytic performance\textsuperscript{4,6,7}. The composite approach relies on exploiting band-edge offsets, directing the electrons and holes into different materials, thereby providing spatial separation.

Recently, many publications have coupled BiVO\textsubscript{4} with other metal oxides such as Bi\textsubscript{2}O\textsubscript{3}\textsuperscript{8,9}, V\textsubscript{2}O\textsubscript{5}\textsuperscript{10,11}, TiO\textsubscript{2}\textsuperscript{12,13}, WO\textsubscript{3}\textsuperscript{11,14–16}, CdS\textsuperscript{17}, CuCr\textsubscript{2}O\textsubscript{4}\textsuperscript{18} and CuWO\textsubscript{4}\textsuperscript{19} for water purification and water spitting applications. The results show that the semiconductor composite photocatalysts were more active than individual catalysts for all photocatalytic degradation of organic pollutants - notwithstanding the fact that it is less likely that composites providing lower photocatalytic performances would be published. While most of these reports on composite catalysts acknowledge the role of band edge offsets, detailed investigations of reaction mechanisms are often not undertaken, nor has the nature of these energy offsets been thoroughly scrutinized\textsuperscript{8,10,13,18,20}.

Here we present a systematic study, pairing BiVO\textsubscript{4} with three different metal oxide semiconductors to create different offsets scenarios. CeO\textsubscript{2}/BiVO\textsubscript{4}, TiO\textsubscript{2}/BiVO\textsubscript{4} and WO\textsubscript{3}/BiVO\textsubscript{4} provide these different valence band (VB) and conduction band (CB) edge offsets, with the CB and VB potential edges of BiVO\textsubscript{4} being more positive than those of CeO\textsubscript{2}, in between those of TiO\textsubscript{2}, and more negative than those of WO\textsubscript{3} as shown in Fig. 1\textsuperscript{6,7,20–22}. These
materials are selected based on literature values, as it is expected that this will result in different charge transfer (CT) processes being able to take place. In each case BiVO₄ has the narrowest bandgap and hence the broadest absorption, so the total amount of light harvested is consistent for each of the composites. As the above band edge potentials are obtained from different sources, and measured under different conditions, optical band gap and Mott-Shottkey measurements are conducted in order to confirm the predicted offsets.

A number of mechanisms for photocatalytic degradation of dyes by semiconductors are summarised in Fig. 2, including (1) direct photolysis of dyes (2) dye photosensitization (i.e. charge injection from a photoexcited dye leaving unstable dye anion/cation) and (3) photocatalytic degradation of dyes attack by radical generated by photoexcitation of semiconductor (SC)²²–²⁵. Typically direct photolysis is very slow, impractical as a means to
remove organic contaminants from waste water, and indeed is the reason why researchers look towards using photocatalysts to enhance degradation rates\(^2\). Figure 2a shows schematically how mechanism (1) operates. It is expected that mechanism (1) should be independent of the catalyst used, or the percentage of each catalysts used in composite systems, provided there is no light harvesting competition (Methylene Blue, MB, absorbs most strongly at 664 nm, well beyond the absorption onset of BiVO\(_4\)).

There are two variants of mechanism (2) which may occur, depending on the redox potentials of the dye compared to the band edges of the catalyst. Mechanism (2i) is photoanodic sensitization, with the excited dye injecting an electron into the semiconductor leading to an oxidized radical cation (Dye\(^+\)), while (2ii) is photocathodic sensitization, generating a reduced radical dye (Dye\(^-\)). Furthermore, these injected charges may lead to generation of other radical species. The chemical driving force between the dye redox potentials and those of the semiconductor will largely determine the rate of mechanism (2), and as such, with everything else being equal, should be proportional to the geometric mean of the components in composites.

Degradation mechanisms (3i-vi), shown in Fig. 2b, rely on photoexcitation of the semiconductor. Generated \(h^+\) and \(e^-\) pairs (in the VB and CB of the semiconductor respectively) then react either directly (3i and 3ii) or generate radical intermediate species, which can degrade organic species such as the aforementioned dyes (3iii–3vi). There are a number of reactions which may take place, once again depending on the energies of the semiconductor band edges and the environment in which it exists\(^25\).

\[
\begin{align*}
(3i) & \quad e^-_{\text{CB}} + \text{Dye} \rightarrow \text{Dye}^* \quad (\text{Dye dependent}) \\
(3ii) & \quad h^+_{\text{VB}} + \text{Dye} \rightarrow \text{Dye}^+ \quad (\text{Dye dependent}) \\
(3iii) & \quad e^-_{\text{CB}} + \text{O}_2\text{(aq)} \rightarrow \text{O}_2^* \quad (\sim 0.18 \text{ V vs NHE}) \\
(3iv) & \quad e^-_{\text{CB}} + \text{O}_2\text{(aq)} + \text{H}^+ \rightarrow \text{HO}_2^* + \text{H}^+ \quad (\sim 0.10 \text{ V vs NHE}) \\
(3v) & \quad h^+_{\text{VB}} + \text{OH}^- \rightarrow \text{OH}^+ \quad (\sim 1.99 \text{ V vs NHE}) \\
(3vi) & \quad h^+_{\text{VB}} + \text{H}_2\text{O} \rightarrow \text{H}^+ \text{OH}^+ \quad (\sim 2.73 \text{ V vs NHE})
\end{align*}
\]

Thus, the degradation will greatly depend on the adsorption of the dye, \(O_2\), \(OH^-\), \(H^+\) and/or \(H_2O\) on the surface of semiconductor. Photogenerated \(e^-\) and \(h^+\) can of course also recombine (either radiatively or non-radiatively) within the material. It is therefore beneficial to increase the lifetimes of these species to increase the probability that they will participate in one of the above reactions (3i–vi). Mechanisms in this third family may display a synergistic response, where composites can lead to higher reaction rates than either of the two component materials.

In addition to examining rates of photocatalytic degradation for the different heterostructures, in this study, we also examine the mechanisms. This is done in two ways: firstly, through reactive species quenching studies, to differentiate between mechanisms involving \(OH^*, O_2^*, h^+, e^-\) and secondly with action spectra, taken to deconvolute the responses of the constituent materials. Additionally, a range of physical characterization techniques were employed, such as X-Ray Diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Mott-Schottky experiments, and Scanning Electron Microscopy (SEM).

Rhodamine B (RhB) and Methylene Blue (MB) are commonly used as model dyes for photodegradation experiments, being broadly representative of organic compounds in their class\(^22, 24\), while being strongly light absorbing (making the remaining concentration easy to monitor by UV-Vis spectroscopy). In addition, since they absorb visible light, mechanisms (1) - direct photolysis\(^25\), and (2) - sensitization may occur in these systems, in addition to (3). Photoexcited MB can undergo a one electron reduction by other MB molecules to produce Leuco-methylene blue (MB/MB\(^-\) = –0.23 V vs. NHE)\(^23\).

**Results**

WO\(_3\)/BiVO\(_4\), TiO\(_2\)/BiVO\(_4\) and CeO\(_2\)/BiVO\(_4\) composite powders, along with the respective pure materials, were synthesized by wet chemical methods with different mole ratios (1:4, 2:3, 1:1, 3:2 and 4:1), and used to produce photocatalyst films on glass by a doctor blading method\(^29\). In a preliminary study, the photocatalytic activities these investigated by degradation of MB and RhB under visible light irradiation, (Fig. S2). It should be noted that in each case, the composites outperformed the individual component materials, but did not contain any significant doping or any a mixed oxide phases.

The crystal structures of the composites were characterized by XRD, as shown in Fig. 3, with each XRD pattern showing only characteristic diffraction peaks of monoclinic BiVO\(_4\) and either monoclinic WO\(_3\), tetragonal TiO\(_2\) (anatase) or cubic fluorite CeO\(_2\) respectively, as expected. XRD patterns of the individual component materials can also be found in Fig. S3. Furthermore, XPS analysis was carried out to study the surface chemical composition of the above composites, and take a more detailed look at the interactions between BiVO\(_4\) and the other metal oxide in each of the composites, as shown in Figs S4–S6. Due to proximity, electronic interactions were observed for these composites when examined by XPS\(^30–34\). It was therefore concluded, from XRD and XPS that these systems were intimately formed composites, but did not contain any significant doping or any a mixed oxide phases.

The morphologies of WO\(_3\)/BiVO\(_4\), TiO\(_2\)/BiVO\(_4\) and CeO\(_2\)/BiVO\(_4\) composite powders and films were investigated using SEM (Fig. 4), with films shown to be highly porous and approximately the same thickness, ~2.8 \(\mu m\), by cross-sectional SEM (Fig. 4c). In line with profilometry values mentioned previously. In each case, the two component materials appear to be well distributed among each other, as it particularly evident in the Energy Dispersive X-Ray Spectroscopy (EDS) maps. EDS data shows Bi and V tracking with one another, as expected, while other regions are rich in either W, Ti or Ce respectively, corresponding to WO\(_3\), TiO\(_2\) or CeO\(_2\) particles in...
the relevant composites. The scale of these differences suggests again that there are well-formed composites, with each containing image (Fig. 4a,d,g) two distinct materials in close proximity to one another. Further analysis of EDS (Figs S7–S9) is included in the supplemental information, along with TEM images (Fig. S10).
The mechanisms of photocatalytic degradation of MB and RhB, by BiVO$_4$/WO$_3$, BiVO$_4$/TiO$_2$, and BiVO$_4$/CeO$_2$ were investigated by an indirect chemical probe method, with active species scavengers (see Fig. 5). Normally in the photocatalytic oxidation process, organic species (notably double bonds) are attacked by active species, including holes ($h^+$), hydroxyl radical (HO$^\bullet$), and/or superoxide anion radical (O$_2$$^•$−). As mentioned, IPA, BQ and EDTA were introduced into photocatalysis experiment as scavengers of HO$^\bullet$, O$_2$$^•$− and h$^+$, respectively. The photocatalytic degradation rate constant ($k_{app}$) for the composites and pure materials (both for MB (Fig. 5a) and RhB (Fig. 5b)), with the above quenchers (1 mM) were investigated under simulated solar irradiation.

The addition of BQ almost completely quenched the dye degradation of both the pure BiVO$_4$ and CeO$_2$ indicating that O$_2$$^•$− is the major active species in these systems. For the photodegradation of dyes with the TiO$_2$ and WO$_3$, a large suppression was noted upon the addition of IPA. As such, HO$^\bullet$ was shown to be the main oxidation specie in pure TiO$_2$ and WO$_3$ photocatalysis systems. The photocatalytic systems with added EDTA showed similar degradation rates compared to the system without scavengers, suggesting a limited role played by holes in the valence band. This may, in part, due to these reactions proceeding via reactions with OH$^−$, which is presumed to be in short supply at pH 5.

Additionally, these studies suggest multiple mechanisms are at play in the degradation of MB and RhB dyes, with further studies being done to confirm this. Two major active species in the photodegradation process of MB and RhB dyes in the presence of TiO$_2$/BiVO$_4$ composite were seen, O$_2$$^•$− and HO$^\bullet$, while the main species of CeO$_2$/BiVO$_4$ and BiVO$_4$/WO$_3$ composite systems were O$_2$$^•$− and HO$^\bullet$, respectively. The generation of these radical species is explained in the context of their band edge energies, with the conduction band edge energies confirmed by Mott-Schottky measurements (Fig. S11) and valence band edges inferred based on optical bandgaps (see Fig. 6, Fig. S12 and Table S2). These experiments also highlight the possibility of a photocatalyst system being poisoned, a challenge which must be addressed in any real-world application of this technology.

Figure 6 shows the normalised rate constants for photodegradation of MB dye over the different photocatalysts under monochromatic light (using band pass filters) along with their absorption spectra. MB was chosen for this study as its absorption has little overlap with that of the photocatalysts in question, as opposed to RhB. As expected, in the absence of any catalyst (Fig. 6a) MB degraded most rapidly under 650 ± 20 nm light, close to its maximum absorption (664 nm) as a result of direct photolysis (mechanism 1, from Fig. 2a). A similar response to these wavelengths were seen with all catalysts as well. As was mentioned previously, mechanism (1) degradation should be largely independent of the catalyst used, while mechanism (2, specifically 2i in this case)
will be influenced by the chemical potential of free electrons in the CB. It is therefore concluded that that mechanism (2) plays a minor role, if at all, in the total photodegradation process here.

The absorption onsets of the WO$_3$, TiO$_2$ and CeO$_2$ were found to be 500, 390 nm and 435 nm respectively, while the absorption onset of all composites were dictated by that of BiVO$_4$, at about 525 nm (shown in Fig. 6b–d). It is seen that the main mechanism of MB degradation in each case is due to the photogeneration of reactive radical species. As mentioned above, composite formation is shown to have synergistic effect on degradation rates, suggesting effective interactions between the various metal oxide species.

For each composite, the responses to light of higher than band gap energies were enhanced as compared to the individual components, however this was more dramatic for some cases than others. As mentioned previously, BiVO$_4$ was selected as the common material as this results in equivalent total light harvesting for the composites. This hypothesis was validated looking at the absorption onsets of the composites, which were all indeed close to that of pure BiVO$_4$. This also provides us with the ability to deconvolute the responses of the coupled materials. At 500 nm BiVO$_4$ absorbs, whereas CeO$_2$ or TiO$_2$ do not (this is within the range of the absorption onset for WO$_3$, however direct comparison the response to this 500 nm light, as compared to 400 nm or 450 nm, where WO$_3$ more strongly absorbs light, is illustrative). Interestingly, while all composites showed a synergistic response at this wavelength, in the case of TiO$_2$ and WO$_3$, shorter wavelengths (400 and 450 nm) result in less marked differences as compared to pure BiVO$_4$. On the other hand, CeO$_2$ displays similar synergistic behaviour at all wavelengths from 400 to 500 nm.

Based on the combined results of quenching studies, monochromatic illumination Mott-Schottky experiments (Fig. S11) and optical band gap measurements (Fig. S12), the primary degradation mechanisms are proposed for the individual materials and WO$_3$/BiVO$_4$, TiO$_2$/BiVO$_4$, and CeO$_2$/BiVO$_4$ composites and are shown in Fig. 7. As mentioned, the main photodegradation mechanism seen with BiVO$_4$ involves the transfer of a photoexcited e$^-$ from the CB of BiVO$_4$, along with a proton, to adsorbed an O$_2$ on the semiconductor surface, generating HO$_2$$^\bullet$.

Meanwhile, quenching studies showed OH$^\bullet$ to the only major reaction species for the pure WO$_3$ photocatalyst system, which be produced by oxidation at VB of WO$_3$. As OH$^-$ exists only at low concentrations in slightly acid conditions, the photocatalytic activity exhibited here was lower than other materials. For the WO$_3$/BiVO$_4$ composite, (Fig. 7e) the CB and VB band edges of BiVO$_4$ are more negative than the CB and VB of the other component. Both BiVO$_4$ and WO$_3$ can be activated by visible light irradiation and generated e$^-$ and h$^+$ pairs, although at 500 ± 20 nm, the relative portion of light harvested by the WO$_3$ should be considerably less compared to BiVO$_4$ than under 400 or 450 nm illumination.
According to the band edge analysis, electrons transferred to the CB of WO$_3$ cannot reduce O$_2$ to form radical species, as they can from the BiVO$_4$ CB. This is reflected in quenching studies, with the deactivation of the O$_2$•$^-$ species mechanism in BiVO$_4$ as it is paired with WO$_3$, representing an unintended consequence of composite formation. On the other hand, the photo-generated h$^+$ at the VB of WO$_3$ can transfer to the VB of BiVO$_4$, which can oxidize H$_2$O and HO$^-$ to HO$.^*$ Adding to the complex combination of effects in the composite, the dye is seen to have a very strong affinity towards WO$_3$. This is further explored by inspection of adsorption/desorption equilibrium of the dye, as measured in the dark (MB in Fig. 8 and RhB in Fig. S13), which shows the affinity of the dye towards WO$_3$ to be quite strong as compared to BiVO$_4$. In spite of an overall increased photocatalytic
performance of the composite, as compared to pure WO₃ or pure BiVO₄, it can be seen that the mechanism of this enhancement is not straight forward. A similar trend was seen for RhB (see Fig. S13).

The role of surface area and isoelectric points (IEP) was explored (Fig. 8 above, as well as Fig. S14). This shows dye loading to be (1) highly dependent upon the materials’ isoelectric point and (2) for composites, loading is close to a stoichiometric mixture of the loading of the individual component materials. The effect of the affinity for the dye for the various metal oxides is pivotal towards our understanding of the photocatalytic behaviour of composites, as described in the following paragraphs.

Under illumination TiO₂ can generate HO• by reaction of adsorbed H₂O and h⁺ in its VB. Additionally, adsorbed O₂ can produce O₂•−, by reaction with free e− in the CB. Figure 7f shows the mechanisms observed in BiVO₄/TiO₂ composites, where the CB and VB of BiVO₄ are both located between the CB and VB of TiO₂. This represents an interesting case, particularly under 450 nm and 500 nm illumination, where only BiVO₄ is photoexcited and there are no obvious pathways whereby CT to TiO₂ can occur. Photocatalytic performance is however substantially higher than for pure BiVO₄. This appears to again stem from the affinity of the dye for TiO₂, whereby a high concentration of these dyes is maintained in proximity to the BiVO₄ catalyst, which is the primary producer of the active radical species. This affinity is seen in the dark adsorption/desorption equilibrium (Fig. 8) and explained by the by the zeta potential of TiO₂ (Fig. S14). Thus, the major process of this system should be driven by the visible light havering of BiVO₄ which can produce HO• and/or O₂•− at its CB.

As CeO₂ has a higher CB edge potential than BiVO₄, free electrons have a substantial free energy to generate O₂•− from O₂, which was seen to be the main photocatalytic mechanism at play here (Fig. 7d). The comparatively low photocatalytic activity of CeO₂ (versus BiVO₄) is in part attributed to low visible light absorption. 400 nm monochromatic illumination shows however that this is not the only factor, along with dark adsorption/desorption measurements (Fig. 8) which reveal the low affinity of the dye for CeO₂, despite its high surface area. As seen in Fig. 7g, the CB and VB potential edges of BiVO₄ are more positive than those of CeO₂. The tendency of CT is that photoexcited e− in the CB of CeO₂ can be transferred to BiVO₄, where they can react with absorbed O₂ to create O₂•− radicals. From the quenching studies, HO• was also observed to play a role in this system, suggesting that these HO• were probably generated from intermediate species and/or the generated O₂•− and HO• radicals.

Therefore, the main mechanism is production of HO• at the VB of the BiVO₄ in the composite that leads to showing the lowest photocatalytic activity as compared to the CeO₂/BiVO₄ and TiO₂/BiVO₄ composites.

Discussion

A series of composites were constructed, containing WO₃, TiO₂ or CeO₂ with BiVO₄. This last component ensured each system had similar overall light harvesting. XRD, XPS, SEM and TEM analyses confirm the formation of the composite without significant doping. Furthermore, highly porous films were formed, with a good dispersion of the different materials among each other.

Superior photocatalytic performance for degradation of MB and RhB under simulated solar light irradiation was observed for all composites, relative to their component materials. Monochromatic illumination and active species quenching studies were conducted and revealed a great deal of information about the different routes by which radical species were produced, leading to the degradation of these dyes. Quenching studies, indicated that O₂•− is a main reactive specie generated by CeO₂/BiVO₄ systems, while BiVO₄/WO₃ primarily degraded dyes via HO• and both O₂•− and HO• were active for the TiO₂/BiVO₄ composite.

Typically enhanced free carrier lifetimes resulting from a spatial separation of charges in different (neighbouring) materials is cited as a reason for enhanced performance, however here we see a number of other factors also had a bearing on the behaviour of composite systems. Specifically, it was seen that the affinity of the dye to the partner semiconductor plays a major role as it provides a high local concentration, where generated radicals have a higher probability of being active as compared to in the general solution. This was demonstrated clearly in the case the BiVO₄-TiO₂ composite, under 450 and 500 nm illumination of where no CT mechanisms are favourable, yet the degradation rate constant is roughly twice as large as for pure BiVO₄. The WO₃-BiVO₄ composite was also seen to be an interesting case, with the band edge configuration deactivating one radical species generation pathway. Again, the overall performance increased, which again be attributable to high dye affinity for WO₃.

This study highlights the complexities of composite design for photocatalysis, and the need to consider a range of factors, such as zeta potential and surface area, when designing new systems. It also demonstrated that band edge offsets can lead to deactivation of radical species generating pathways, as well as the more desirable increase in free charge carrier lifetime. We hope that it can serve as a basis for further design of new composite materials for water purification and other applications.

Methods

Preparation of photocatalyst powder. The synthesis of all photocatalysts were carried out by solution phase synthetic methods. For the synthesis of BiVO₄ powder, bismuth nitrate and ammonium vanadate in dilute nitric acid solution were used as starting precursors for precipitation at room temperature. CeO₂/BiVO₄ and TiO₂/BiVO₄ composites were prepared by two-step methods. Firstly, BiVO₄ powder was synthesised by a precipitation method. Subsequently the BiVO₄ powder was added into either cerium nitrate or titanium isopropoxide solutions to prepare composites by precipitation or sol-gel methods, respectively. BiVO₄/WO₃ composites were also synthesised by a two-step precipitation method, where WO₃ powder was first synthesised using tungsten nitrate as the starting material. The WO₃ powder was added into a solution with Bi and V precursors. The choice of synthetic order relates to pH regulation for each step and stability of the partner material under these conditions. Detailed descriptions of the synthesis of each of the CeO₂/BiVO₄, TiO₂/BiVO₄ and BiVO₄/WO₃ composites in the supporting information.
Fabrication of photocatalyst films. All films for photocatalytic testing and electrochemical measurements were prepared by a doctor blading technique. Briefly, 0.5 g of the photocatalyst powder was used, along with 75 µL Triton X-100, 25 µL acetic acid and 4 mL ethanol. The slurry was ground with a mortar and pestle for 10 min, during which ethanol was added in small aliquots to wash and scatter larger agglomerates. The paste was then sonicated for a further 30 min. Films were obtained by blading the slurry (~100 µL) on either glass slides (film size = 20 mm × 40 mm) for photocatalytic experiment or (~12.5 µL) on FTO glass working electrodes (film size = 10 mm × 10 mm) for Mott–Schottky experiment. This was carried out on a heated (50 °C) surface, using Scotch Tape (3 M, 50 µm) as a spacer. These films were then annealed in air at 450 °C for 2 h, to produce mechanically stable films. The thicknesses of the resulting films were 2.8 ± 0.1 µm, as measured with a stylus profilometer (VeecoDektak 150).

Physical characterization of photocatalyst materials. X-Ray Diffractometry (JDX-3530, JEOL, Japan) was completed using Cu Kα radiation (λ = 1.546 nm). The detection range was 10° and 70° with the step size of 0.2° (2θ/s) in continuous scanning mode. Film morphologies were investigated by a Scanning Electron Microscope (SEM, JSM-7500FA, JEOL, Japan) with the accelerating voltage and emission current as 5.0 kV and 0.2° (2θ/s) respectively. The chemical composition and electron structure of the bare CeO₂, BiVO₄ and BiVO₄/CeO₂ composite were measured by X-ray photoelectron spectroscopy (XPS, PHOIBOS 100 hemispherical energy analyser from SPECS) using Al Kα radiation (1486.6 eV) in fixed analyser transmission mode. The binding energies were calibrated with reference to C 1 s line at 284.6 eV for hydrocarbon contamination.

Films were optically characterized using a Shimadzu 3600 UV-Vis-NIR spectrophotometer, with integrating sphere attachment. Transmission and reflection measurements were made in order to determine the absorption.

Photocatalytic testing. Photocatalytic activities of the synthesized photocatalyst powder and films were studied by the degradation of either Rhodamine B (~25 µM, RhB) or methylene blue (~50 µM, MB) solutions under simulated solar illumination (AM1.5 G, 1 sun equivalent, 100 mW·cm⁻²). For monochromatic experiments, ±20 nm band pass filters were applied to the above light source.

Photocatalyst films were placed put in a reactor with the dye solution. Prior to irradiation, the films were left overnight in the dye solution under continuous magnetic stirring in order to attain an adsorption/desorption equilibrium. At irradiation time intervals of 30 min, the dye solution was collected and measured using an UV-vis spectrophotometer (Agilent 8453 photodiode array). After that, the collected solution was put back into the reactor, and the photodegradation reaction resumed (<3 min intermission).

An indirect chemical probe method was employed to investigate the mechanisms of dye degradation. Scavengers of various possible active species, including isopropanol (IPA, an HO⁺ quencher), benzoquinone (BQ, O₂⁻ quencher) and ethylenediamine tetra acetica acid (EDTA, a h⁺ scavenger), were added at 1 mM during the photoreaction.

Each experiment was repeated in triplicate, with the average value shown along with one standard deviation as an error bar.

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