NaₓWO₃ + TiO₂ nanocomposites as plasmonic photocatalysts for the degradation of organic dyes

Levi Tegg and Vicki J Keast
School of Mathematical and Physical Sciences, University of Newcastle, Callaghan, NSW 2308, Australia
E-mail: Levi.Tegg@uon.edu.au

Keywords: plasmonics, tungsten bronzes, photocatalysis

Abstract

The combination of plasmonic metal nanostructures with semiconductor photocatalysts can improve their photocatalytic efficiency by increasing light absorption and aiding in charge separation. Metallic NaₓWO₃ has been shown to be strongly plasmonic and offers a readily synthesized and low-cost replacement for the noble metals which are conventionally used in plasmonic photocatalysts. In this work, a range of NaₓWO₃ + TiO₂ nanocomposites were fabricated. Composites containing both semiconducting (x < 0.25) and metallic (x > 0.25) NaₓWO₃ were prepared. The degradation of rhodamine 6G (R6G) under visible and near infrared (NIR) light illumination was observed only when NaₓWO₃ and TiO₂ were both present in the composite. Photocatalytic activity was generally higher in metallic samples than in semiconducting ones, but the sample with the highest activity had a mixture of both. This suggests that a combination of interband transitions and plasmonics-enhanced processes can be used together to catalyse reactions.

1. Introduction

Since the discovery by Fujishima and Honda that n-type TiO₂ can be used as a photocatalyst to split water into \( \text{H}_2 \) and \( \text{O}_2 \) [1] there has been an enormous effort into the development of semiconducting photocatalysts [2, 3]. A global transition away from fossil fuels requires the development of storage and transport fuels, and the direct production of hydrogen from sunlight offers enormous potential to address this need. Furthermore, photocatalysts can be used in other important environmental applications such as CO₂ reduction and the degradation of environmental pollutants [2, 4–8].

The photocatalytic process starts with the photoexcitation of electron-hole pairs in the semiconductor, followed by charge separation, and then the migration of carriers to the surface where they can act as reducing or oxidizing agents in the desired chemical reactions. Recombination of the electrons and holes, either in the bulk or at the surface, will decrease the photocatalytic activity. The energy of the valence and conduction band edges of the semiconductor, relative to the redox potentials of the adsorbates, will govern the probability and rate of charge transfer and therefore photocatalytic reaction rates. As shown in figure 1, the band edges for TiO₂ satisfy the thermodynamic requirements for the case of photosplitting of water. However, the overpotentials for the evolution of \( \text{H}_2 \) and \( \text{O}_2 \) on the surface means that \( \text{H}_2\text{O} \) cannot be decomposed by a clean TiO₂ surfaces and it requires the presence of co-catalysts such as Pt and RuO₂ or sacrificial species such as ethanol [2]. The band edges of TiO₂ are well located for the reduction of \( \text{O}_2 \) and for the oxidation of surface \( \text{H}_2\text{O} \) and hydroxyl groups to generate reactive oxygen species (ROS), making it a suitable candidate for the degradation of pollutants [4].

The major limitation of TiO₂, along with most of the semiconductor photocatalysts, is poor solar energy utilization due to the large bandgap of \( \approx 3.2 \) eV. Only photons with energy greater than this can excite electron hole pairs, but this constitutes only \( \approx 4\% \) of the available solar spectrum [12]. TiO₂ is also limited by high electron-hole recombination rates. There has been an extensive search for new materials to enable high efficiency visible light photocatalysis. These include two-step photoexcitation (Z-scheme) using semiconductor heterostructures or by doping and/or band engineering to achieve a single visible light photocatalyst [3, 13].
Despite its limitations, the low cost, non-toxicity and high photocatalytic stability of TiO$_2$ offers important advantages over many other systems.

Recently, the combination of noble metal plasmonic nanostructures with photocatalytic semiconductors has emerged as alternative approach to enable visible light photocatalysis. Metal nanostructures are capable of sustaining resonant oscillations of the valence charge under electromagnetic illumination, called a localized surface plasmon resonance (LSPR), when the energy of the incoming photons matches the plasmon resonance energy of the nanostructure. There are numerous applications that take advantage of the highly localized and enhanced electric field associated with the LSPR [14–16]. The past decade has seen a great deal of interest in the possibility of plasmonic nanoparticles being combined with semiconductors to achieve high-performance photocatalysis [17, 10, 18, 19]. A metal nanoparticle in contact with TiO$_2$ can generate a Schottky barrier that acts as an electron trap and therefore enhance photocatalytic efficiency by reducing recombination rates. However, the highest rate enhancements have been observed at photon energies corresponding to the LSPR resonances indicating an involvement of the LSPR in the increased photocatalytic activity [10].

There are three mechanisms proposed for how the LSPR enhances photocatalytic reactions [10, 20, 21]. The first is that the plasmon resonance injects electrons into the TiO$_2$ surface. The plasmon resonance is a collective oscillation of many valence electrons at the Fermi level, therefore these electrons cannot directly drive the redox reactions. However, plasmon resonances can decay via the generation of electron-hole pairs in the metal and those hot carriers can then be injected into the TiO$_2$ surface if they have sufficient energy to overcome the Schottky barrier. Photocatalytic enhancement is also observed when the metal nanoparticles are not in contact with the semiconductor. In this scenario the strongly localized near fields associated with the LSPR acts to increase the rate of electron-hole generation. Importantly, these electron hole pairs are generated near the surface, reducing the probability of recombination before participating in the redox reactions at the surface. This mechanism requires overlap between the plasmon resonance energy and the semiconductor photoexcitation energy and so, therefore, likely relies on the presence of defect states within the bandgap of TiO$_2$. Finally, the strong optical scattering associated with LSPRs will increase the optical path length as light passes through the photocatalytic device. The question of the relative importance of the different mechanisms is not yet fully resolved and will depend on the details of the materials and morphology of the specific plasmonic photocatalyst composite [10].

Despite the substantial improvements in photocatalytic performance that have been achieved with noble metal-semiconductor composites, the high cost of the noble metals and the complex fabrication routes are a disadvantage. Cheaper, more readily fabricated alternatives would be preferred. The sodium tungsten bronzes (Na$_x$WO$_3$, 0 $\leqslant x \leqslant$ 1) have already been identified as a low-cost, high performance, readily fabricated alternative plasmonic material [21–23]. They are semiconducting when $x < 0.25$ and metallic for $x \geqslant 0.25$, and relevant redox potentials [4, 10]. The DOS are shifted so that the calculated $E_F$ matches the experimental work function for that value of $x$ [11].

Figure 1. Calculated density of states (DOS) and Fermi energies ($E_F$) of c-Na$_x$WO$_3$ across $0.250 \leqslant x \leqslant 0.875$ compared with the band edges of TiO$_2$ [9], and relevant redox potentials [4, 10]. The DOS are shifted so that the calculated $E_F$ matches the experimental work function for that value of $x$ [11].

2
with the bulk plasmon resonance increasing in frequency and intensity with $x$ [22]. It is expected that a Na$_x$WO$_3$ + TiO$_2$ composite would be an effective photocatalyst. Hexagonal (h-) Na$_x$WO$_3$ [24] and h-Cs$_x$WO$_3$ [25, 26] have previously been identified as visible light photocatalysts on their own and also as a h-Cs$_x$WO$_3$/WO$_y$ composite [27]. In the latter work the h-Cs$_x$WO$_3$ in the composite was probably a semiconducting phase and therefore this would not be considered a plasmonic photocatalyst. Plasmonic resonance intensities and frequencies both increase with $x$ in Na$_x$WO$_3$, which is advantageous for the photocatalytic efficiency of the plasmonic photocatalyst. The hexagonal crystal structures are limited to $x \leq 0.33$ [28] and so cubic (c-) Na$_x$WO$_3$ would be preferred as the plasmonic component. It has been demonstrated that a c-Na$_x$WO$_3$–WO$_2$ composite has a significantly increased hydrogen evolution rate for water splitting than WO$_2$ alone, although the role of plasmonic excitation in that process was not discussed in that work [29]. In this work we prepare Na$_x$WO$_3$ + TiO$_2$ nanocomposites for a range of $x$ values and compare their photocatalytic efficiency for the degradation of rhodamine 6G (R6G) dye under visible and near infrared (NIR) light illumination.

2. Methods

2.1. Synthesis

Na$_x$WO$_3$ samples with nominal compositions of $x_n = 0.1, 0.2, 0.3, 0.4, 0.6$ and $0.8$ were prepared by a furnace-assisted technique, using the same method reported previously [23, 30]. Briefly, powders of Na$_2$WO$_4$•2H$_2$O (VWR, > 99%), WO$_3$ (Sigma-Aldrich, 99.9%) and W (Aldrich, > 99.9%) were weighed in the appropriate ratios [21] and mixed using a mortar and pestle. The powders were pressed under 20 MPa of pressure into a pellet, and fired individually in a vertical tube furnace for 90 s. The $x_0 = 0.1$ and 0.2 samples were fired at 1000 °C, the $x_0 = 0.3$ and 0.6 at 900 °C, the $x_0 = 0.4$ at 1050 °C, and the $x = 0.8$ at 850 °C. Extending on our previous work [23], we have found that these temperatures are optimum for producing phase-pure c-Na$_x$WO$_3$ nanoparticles.

Na$_x$WO$_3$ + TiO$_2$ composites were prepared by mixing 0.100 g of Na$_x$WO$_3$ with 0.010 g of TiO$_2$ (Degussa P25, ≥ 99.5%) in 0.5 ml of ethanol. The suspensions were stirred vigorously at room temperature for several hours, then pipetted onto glass substrates and dried at 60 °C. The samples were rinsed in ethanol to remove any loose powder, then soaked in a solution of R6G chloride (Exciton Inc.) in ethanol overnight in the dark. Previous reports [25, 31, 32] have shown that dyes such as R6G and methylene blue have high affinity for tungsten bronze surfaces, so the samples were pre-saturated in R6G to reach an adsorption equilibrium before their use in photocatalysis experiments.

2.2. Photocatalysis

After soaking overnight, the samples were placed in fresh R6G+ ethanol solutions in glass vials. It was found that the Na$_x$WO$_3$ + TiO$_2$ samples did not adhere to the glass substrates when H$_2$O was used as a solvent, so ethanol was used instead. The initial R6G concentration was $\approx 9 \times 10^{-6}$ mol L$^{-1}$, with a peak absorbance of $A \approx 1$ at $\lambda = 530$ nm. Four samples at a time were irradiated with a Zeiss HAL 100 tungsten–halogen incandescent lamp with a colour temperature of $\approx 3300$ K. Every $\approx 60$ min, the lamp was switched off and the R6G solution was extracted. Spectrophotometry of the extracted R6G solutions was performed using a Varian Cary 6000 UV–vis. The R6G solutions were analysed across 350 nm–800 nm. After analysis, the R6G solutions were returned to the reactor vials and the lamp was switched back on. One of the samples (Na$_{0.42}$WO$_3$ + TiO$_2$) was re-used in fresh R6G solutions to confirm the chemical stability of the composite. This sample was not soaked or washed before re-use.

2.3. Characterisation

Powder x-ray diffraction (XRD) was performed using a Phillips X’Pert MPD XRD using Cu Kα radiation. The patterns were analysed using the Rietveld method, after phases were identified using the International Crystal Structure Database [33]. The Na content of the c-Na$_x$WO$_3$ phase was found using the relationship between lattice parameter and Na content from Brown and Banks [34], and quantitative phase analyses was performed using the method of Hill and Howard [35]. Samples were prepared for scanning electron microscopy by pipetting the Na$_x$WO$_3$ + TiO$_2$ slurry onto aluminium substrates, then drying. The samples were imaged using the back-scattered electron (BSE) detector of a Zeiss Sigma VP FESEM, with a beam voltage of 15 kV. The optical absorbance of the nanomaterials dispersed in ethanol was measured using a Varian Cary 6000 UV–vis spectrophotometer, using ethanol as a $T = 100\%$ reference.

2.4. Calculation

Density functional theory (DFT) calculations were performed using the linearized augmented plane-wave method, as implemented in WIEN2k [36] and as described previously [21]. Briefly, a $2 \times 2 \times 2$ superstructure of the Pm-3m structure of c-Na$_x$WO$_3$ [34] was constructed where up to 8 Na atoms could be inserted, giving
compositions $0.250 \leq x \leq 0.875$ in $\Delta x = 0.125$ steps. The lattice parameter was set using the linear relation of Brown and Banks [34].

3. Results and discussion

3.1. Electronic structure

Figure 1(a) shows the density of states (DOS) for selected c-Na$_x$WO$_3$ in the metallic composition range [37], $0.250 \leq x \leq 0.875$, calculated using DFT. The energy axis is given with respect to the vacuum level. The vacuum levels for Na$_x$WO$_3$ for each value of $x$ were not calculated using DFT but instead the calculated Fermi energies ($E_F$) were set to a linear interpolation between the experimental work functions measured by Hill and Egdell [11]. Apart from the expected underestimation of the gap between the valence and conduction bands when using GGA exchange correlation potentials, the DOS shown here are similar to those predicted from photoelectron studies [1, 38, 39] and are consistent with previous DFT studies for NaWO$_3$ [40, 41]. The DOS for semiconducting Na$_x$WO$_3$ are not included as DFT calculations do not accurately model Anderson localization which dominates the electronic properties in the very low-$x$ sodium tungsten bronzes [42, 43]. The valence and conduction bands of TiO$_2$ are shown in figure 1(b), along with some important redox potentials in water-splitting and dye degradation [4, 10].

The electronic structure of metallic Na$_x$WO$_3$ can be understood as follows. In the absence of oxygen vacancies, WO$_3$ is a n-type semiconductor with an indirect band gap of $E_g \approx 2.7$ eV [44, 45]. For $x > 0.25$, the inserted Na transfers its 3s electron to the W 5d conduction band and the system becomes metallic, with the work function and free-electron density increasing as more Na is inserted [22, 11, 43, 46]. The DFT calculations demonstrate that the electronic structure and work function of Na$_x$WO$_3$ can be tuned via variations in composition. Furthermore, the energy of the LSPR can also be tuned via compositional changes. Na$_x$WO$_3$ thus holds advantages over conventional noble metals for a plasmonic photocatalytic platform, but also over other M$_x$WO$_3$ as the Na$_x$WO$_3$ system has the widest composition range and flexibility in electronic and optical properties.

3.2. Phase-purity and morphology

Na$_x$WO$_3$ with different values of $x$ were synthesized [23, 30] and composites of Na$_x$WO$_3$ + TiO$_2$ were prepared for use as plasmonic photocatalysts. Figure 2 shows XRD patterns of the as-synthesised Na$_x$WO$_3$ samples with nominal compositions of (a) $x_n = 0.2$, (b) $x_n = 0.3$, (c) $x_n = 0.4$ and (d) $x_n = 0.6$. Also shown are Rietveld refined models and labels for the peaks of identified phases. Table 1 shows the composition of each sample to within $\pm 1$ mol%, as determined from the refined model. With the exception of the $x_n = 0.2$ sample, the prepared Na$_x$WO$_3$ samples are of high purity. All samples are >96 mol% Na$_x$WO$_3$, although in low-$x$ samples there is a mixture between the cubic and the tetragonal-I (TII-) or tetragonal-II (TII-) structures. The XRD
pattern for the $x_n = 0.2$ sample included peaks matched to an unindexed phase with nominal composition $\text{Na}_{0.16}\text{WO}_3$, originally reported by Bamberger and Kopp [47]. Without structural information for the unindexed phase, quantitative phase analysis could not be performed on this sample.

The lattice parameter of the $c$-Na$_x$WO$_3$ phase can be used to determine the Na content, $x_r$, using the relationship of Brown and Banks [34]. When $c$-Na$_x$WO$_3$ is a large molar fraction of the sample, the $x_r$ of $c$-Na$_x$WO$_3$ can be used to approximate the Na content of the entire sample. As shown in table 1, the $x_r$ differs from $x_n$ by less than 0.02 for the samples with $x_n \geq 0.3$. The $x_n = 0.1$ and $x_n = 0.2$ samples contained little $c$-Na$_x$WO$_3$, so for those samples it is assumed that the ‘true’ Na content is close to $x_n$.

Figure 3 shows scanning electron microscope (SEM) images of the fabricated nanocomposites (a) Na$_{0.42}$WO$_3$ + TiO$_2$ and (b) Na$_{0.61}$WO$_3$ + TiO$_2$, captured using the back-scattered electron (BSE) detector.

### Table 1. Composition (mol%) and refined Na content ($x_r$) for samples of different nominal Na content ($x_n$).

| $x_n$ | $x_r$ | mol% |
|-------|-------|------|
|       |       | c-Na$_x$WO$_3$ | TII-Na$_x$WO$_3$ | T1-Na$_x$WO$_3$ | Na$_2$WO$_4$ | Na$_2$W$_2$O$_7$ | W |
| 0.1   | $^a$  | 8    | —   | 92   | —   | —   |
| 0.2   | $^a$  | n/a  | n/a | n/a  | n/a | n/a |
| 0.3   | 0.30  | 77   | 22  | 1    | —   | 1   |
| 0.4   | 0.42  | 90   | 8   | 1    | <1  | 1   |
| 0.6   | 0.61  | 98   | —   | —    | <1  | 1   |
| 0.8   | 0.79  | 96   | —   | —    | 3   | 1   |

$^a$ c-Na$_x$WO$_3$ content of these samples is too low to accurately determine $x_r$, so instead it will be assumed that the actual Na content is the same as the nominal $x$.

$^b$ This sample contained peaks matched to an unindexed phase of nominal composition Na$_{0.16}$WO$_3$ [47], so quantitative phase analysis could not be performed.

3.3. Optical properties

Figure 4(a) shows the absorbance spectra of some Na$_x$WO$_3$ and TiO$_2$ nanoparticle dispersions in ethanol. Consistent with previous reports [23, 51], Na$_x$WO$_3$ with $x > 0.3$ exhibits strong near-infrared and visible extinction due to LSPRs, and strong ultraviolet (UV) absorption due to interband transitions. The Na$_{0.1}$WO$_3$ sample showed no clear plasmon resonance, consistent with its semiconducting electrical and optical properties.
Figure 4. (a) Absorbance spectra of R6G, TiO₂, Na₀.₁WO₃, Na₀.₄₂WO₃ and Na₀.₇₉WO₃ nanoparticles dispersed in ethanol. The absorbance spectra have been normalised and scaled to easily compare the features between spectra. (b) The approximate emission spectrum from a 3300 K blackbody source similar to the lamp used in this study, and the AM1.5 solar spectrum at 37° tilt for comparison.

Figure 5. Absorbance spectra of R6G solutions in ethanol after 5 h of irradiation, with (a) no active material present, (b) TiO₂ only, (c) Na₀.₄₂WO₃ only, and (d) the Na₀.₄₂WO₃ + TiO₂ composite.

[37]. Figure 4(b) shows the AM1.5 solar spectrum at 37° tilt, and the irradiance of a 3300 K blackbody source similar to the lamp used in the photocatalysis experiments described in the next section. The lamp emits most of its energy in the visible and NIR, with negligible emission in the UV. Although simulations predict plasmon responses with peak widths on the order of ≈0.15 eV [21], the broad particle size distribution in these NaₓWO₃ samples (approximately 150–300 nm) leads to a broad NIR response, associated with the sum of the individual responses of many nanoparticles of different sizes [23]. For many applications of plasmonic nanoparticles, such a broad response would negatively affect performance. However, plasmonic photocatalysts benefit from capturing as much of the solar spectrum as possible, so the broad NIR response of the NaₓWO₃ nanoparticles is desirable.

3.4. Plasmonic photocatalysis

The photocatalytic properties of the NaₓWO₃ + TiO₂ nanocomposites were investigated by submerging the samples in a solution of R6G in ethanol, and irradiating using a ≈ 3300 K incandescent lamp. Figure 5 shows the absorbance spectrum of the dye solution around the ≈530 nm R6G absorption peak with increasing irradiation time, when (a) no active material was used, (b) with TiO₂ only, (c) with Na₀.₄₂WO₃ only, and (d) with the Na₀.₄₂WO₃ + TiO₂ composite. Negligible activity is observed when no active material is present and when the TiO₂ and Na₀.₄₂WO₃ are used separately, but when used together as a composite the absorbance peak associated with R6G decreases, signalling the degradation of the dye. TiO₂ is a high-performance photocatalyst on its own, but the lack of ultraviolet radiation in the incident spectrum means there is no activity when it is used in isolation. Although the Na₀.₄₂WO₃ is highly absorbing in the visible and NIR, its metallic properties make it unsuitable for photocatalysis by itself. Only when the two are used together in a plasmonic-photocatalytic composite is there a change in the concentration of the dye with irradiation time.

From Beers law,

\[ A_{\text{max}} = \varepsilon I C \]  

the peak absorption \( A_{\text{max}} \) from an analyte of concentration \( C \) is proportional to the path length \( l \), and the molar absorptivity of that analyte (\( \varepsilon = 11.6 \times 10^3 \cdot \text{mol}^{-1} \cdot \text{cm}^{-1} \) for R6G [52]). If it is assumed that the degradation of the dye is a first-order reaction, then concentration of the dye with time \( t \) can be modelled by
where $C_0 = C(t = 0)$ is the initial analyte concentration and $k$ is the measured rate constant. Figure 6 shows $C/C_0$ with time for all of the samples studied in this work, with the dashed lines showing fits of the form of equation (2). For clarity, control experiments and samples with low-$x$ are shown in (a), and those with high-$x$ in (b). Dye degradation was only observed when both Na$_x$WO$_3$ and TiO$_2$ were present and illuminated. The $C/C_0$ curves shown are well-described by the first-order reaction shown in equation (2), leading to low uncertainty in the measured rate constant $k$. Although a small amount of UV is produced by the incandescent lamp that was used (figure 4(b)), the lack of photocatalytic activity from TiO$_2$ alone shows that valence-conduction band transitions in the bulk of the TiO$_2$ cannot be the main electron-hole production mechanism.

Figure 6 shows the $C/C_0$ data without any corrections made for differing substrate area ($A$) or lamp irradiance ($I$) between samples. Corrections for these can be made to the measured rate constant if it is assumed they are linearly proportional to the intrinsic rate constant, $k_0$:

$$k_0 = \frac{k}{IA}$$

Figure 7 shows $k_0$ for different control samples and with $x$. The uncertainty shown here includes the variance from calculating $k$ and the uncertainty in measurements of $I$ and $A$. Except for the Na$_{0.30}$WO$_3$ + TiO$_2$ sample, $k_0$ roughly increases with $x$, though the large uncertainty precludes a conclusive statement about the exact relationship at high $x$. Previous researchers have described the photocatalytic mechanisms of M$_x$WO$_3$ in terms of defect states or polarons [24–27], and of M$_x$WO$_3$+semiconductor composites in terms of a ladder scheme.

Figure 6. Variation in dye concentration ($C/C_0$) with irradiation time for various photocatalysts, without corrections for sample area or irradiance. Dots show the calculated $C/C_0$, and the dashed line shows fits of the form of equation (2). (a) shows control samples and samples with low-$x$ Na$_x$WO$_3$, and (b) shows samples with high-$x$ Na$_x$WO$_3$.

Figure 7. Intrinsic rate constants ($k_0$) for the photocatalysis experiments shown in figure 6, calculated using equation (3).
which could desorb and degrade the R6G. If O is also adsorbed, then the ethanol can be oxidised to produce hydroxide free-radicals [\( \text{RCH}_2\text{OH}_{\text{ads}} + 2 \text{H}^+ \rightarrow \text{RCHO} + 2\text{H}_2\text{O} \)].

Regardless of the mechanism, the Na\(_{x}\)WO\(_3\) + TiO\(_2\) composite does not appear to undergo any chemical change. Figures 8(c), (d) shows diffraction patterns of an pristine Na\(_{x}\)WO\(_3\) (as seen in figures 2(b)) and the Na\(_{x}\)WO\(_3\) + TiO\(_2\) composite deposited on glass, after its fourth photocatalysis cycle. Other than the peaks from TiO\(_2\) anatase and rutile, no other new peaks are observed. To within the uncertainty of the measurement,

\[ \Delta A_{\text{max}} < 0.05 \]

Because this change is small compared to the change in concentration due to irradiation (see figure 5), spontaneous degradation of R6G on the Na\(_{x}\)WO\(_3\) or TiO\(_2\) surfaces is unlikely. However, the high adsorption affinity could still play a role as hot electrons or holes could be transferred directly from the TiO\(_2\) or Na\(_{x}\)WO\(_3\) surface to an adsorbed R6G molecule, degrading the dye. Alternatively, noble metal/TiO\(_2\) composites have been shown to oxidise alcohols into reactive hydroxyl radicals [53], which could potentially desorb and enter the solution and corrode the dye. In the absence of oxygen, alcohols adsorbed on TiO\(_2\) surfaces can be oxidised into aldehydes and \( \text{H}^+ \):

\[ \text{RCH}_2\text{OH}_{\text{ads}} + 2 \text{H}^+ \rightarrow \text{RCHO} + 2\text{H}_2\text{O} \]  

If O is also adsorbed, then the ethanol can be oxidised to produce hydroxide free-radicals [53],

\[ \text{RCH}_2\text{OH}_{\text{ads}} + \text{h}^+ + \text{O}_{\text{ads}} \rightarrow \text{RCHOH} + \text{OH}^- + \text{H}^+ \]  

which could desorb and degrade the R6G [25]. As organic dyes are known to adsorb to M\(_x\)WO\(_3\) surfaces, similar mechanisms could take place at the Na\(_{x}\)WO\(_3\) surface.

To investigate the long-term stability of the composites, the Na\(_{0.42}\)WO\(_3\) sample was reused in fresh R6G solutions in repeat photocatalysis measurements. Figure 8(a) shows the variation in \( C/C_0 \) with time after repeated use. After correcting for irradiated area and irradiance, (b) shows there is little change in the rate constant \( k_0 \) after 5 cycles, confirming the high chemical stability of Na\(_{x}\)WO\(_3\).

The corrosion mechanism of R6G in ethanol was not directly explored in this work, as our focus was to investigate whether metallic Na\(_{x}\)WO\(_3\) exhibited similar performance to semiconducting M\(_x\)WO\(_3\) in a composite. Regardless, some general observations and statements can be made. Dyes such as R6G and methylene blue have shown a strong affinity for M\(_x\)WO\(_3\) surfaces [26, 31, 32], but the degradation of the R6G shown here cannot be described by adsorption alone. The uptake of R6G by the samples was measured when compared to the change in concentration due to irradiation of R6G solutions in repeat photocatalysis measurements. Figure 8 shows the variation in \( k_0 \) with time after repeated use. After correcting for irradiated area and irradiance, (b) shows there is little change in the rate constant \( k_0 \) after 5 cycles, confirming the high chemical stability of Na\(_{x}\)WO\(_3\).
the determined $x_\text{h}$ of the two patterns is the same ($x_\text{h} = 0.42$), indicating that if Na$^+$ ions are diffusing out of the Na$_{x}$WO$_3$, it is at a quantity below what is measurable by XRD.

Plasmonic photocatalysis has been widely reported with noble metals (such as Au, Ag, Pd or Pt) acting as the plasmonic material [10, 53], but the low abundance and high cost of these materials limits their use in commercial-scale photocatalysis reactors. Na$_{x}$WO$_3$ is an ideal alternative material for plasmonic photocatalysis, owing to its inexpensive and straightforward synthesis, high chemical stability, and broad NIR and visible LSPRs [23]. We have shown Na$_{x}$WO$_3$ + TiO$_2$ nanocomposites exhibit better photocatalytic performance when the Na content is high. Although the photocatalytic properties of other tungsten bronzes such as Cs$_x$WO$_3$ have also been explored, the low abundance of Cs in the Earth’s crust makes it a less attractive choice in producing low-cost plasmonic photocatalytic composites. Additionally, the low composition limit in the Cs$_x$WO$_3$ system ($x \leq 0.33$ [28]) means the high-quality plasmon responses observed in metallic ($x > 0.25$) M$_x$WO$_3$ [22] cannot be exploited with these materials.

4. Conclusion

By combining the strong optical enhancement of plasmonic nanoparticles with the photocatalytic properties of wide bandgap semiconductors, plasmonic-photocatalyst composites are a promising avenue towards the full utilization of the solar spectrum. In this work, we have examined the photocatalytic activity of Na$_{x}$WO$_3$ + TiO$_2$ nanocomposites under irradiation with visible and NIR light. We observed that R6G dye in ethanol was degraded only when Na$_{x}$WO$_3$ and TiO$_2$ were used together as a composite. In samples with $x < 0.25$, conventional ladder-scheme or polaron absorption can be used to describe the photocatalytic properties, but in metallic samples with $x > 0.25$ these explanations are inadequate and plasmon resonances in the Na$_{x}$WO$_3$ become important. We observed the greatest performance in the Na$_{0.33}$WO$_3$ + TiO$_2$ composite, which we attribute to the combined effects of metallic and semiconducting phases near the metal-to-insulator transition composition. Both Na$_{x}$WO$_3$ and TiO$_2$ are readily synthesised from abundant and low-cost reagents, making them a promising material platform for plasmonic photocatalysis.

Acknowledgments

Tianyi Ma is acknowledged for his insightful discussions. This research was supported by an Australian Government Research Training Program (RTP). The technical support of the Electron Microscope and x-ray Unit at the University of Newcastle (UON) is acknowledged. The work was performed in part at the Materials node of the Australian National Fabrication Facility, a company established under the National Collaborative Research Infrastructure Strategy to provide nano and microfabrication facilities for Australia’s researchers.

ORCID iDs

Levi Tegg https://orcid.org/0000-0003-0496-8716
Vicki J Keast https://orcid.org/0000-0003-4925-5875

References

[1] Fujishima A and Honda K 1972 Nature 238 37
[2] Linsebigler A L, Lu G and Yates J T 1995 Chem. Rev. 95 735–58
[3] Chen X, Shen S, Guo L and Mao S S 2010 Chem. Rev. 110 6503–70
[4] Li X, Xie J, Jiang C, Yu J and Zhang P 2018 Front. Environ. Sci. Eng. 12 14
[5] Magdalane C et al 2018 S. Afr. J. Chem. Eng. 26 49–60
[6] Magdalane C M et al 2019 Journal of Materials Research and Technology 8 2898–909
[7] Kaviyarasu K, Magdalane C M, Jayakumar D, Samson Y, Bashir A K H, Maaza M, Letsholathebe D, Mahmoud A H and Kennedy J 2020 Journal of King Saud University—Science 32 1516–22
[8] Panimalar S, Utharkumar R, Selvi E T, Gomathinayagam P, Inmoohi C, Kaviyarasu K and Kennedy J 2020 Surfaces and Interfaces 20 100512
[9] Bak T, Nowotny J, Rekas M and Sorrell C C 2002 Int. J. Hydrogen Energy 27 991–1022
[10] Zhang X, Chen Y L, Liu R-S and Tsai D P 2013 J. Phys. Chem. B 117 10921–29
[11] Hill M D and Egdell R G 1983 J. Phys. C: Solid State Phys. 16 6205
[12] Ismail A A and Bahnemann D W 2014 Sol. Energy Mater. Sol. Cells 128 85–101
[13] Abe R 2010 J. Photochem. Photobiol. C 11 179–209
[14] Zeng S, Baillargeat D, Ho H-P and Yong K-T 2014 Chem. Soc. Rev. 43 3426–52
[15] Jang Y H, Jang Y J, Kim S, Quan L N, Chung K and Kim D H 2016 Chem. Rev. 116 14992–5034
[16] Stockman M I et al 2018 J. Opt. 20 043001
[17] Linic S, Christopher P and Ingram D B 2011 Nat. Mater. 10 911–21
[18] Ray C and Pal T 2017 J. Mat. Chem. A 5 9465–87
[19] Wu N 2018 Nanoscale 10 2679–96
[20] Hou W and Cronin S B 2012 Adv. Funct. Mater. 23 1612–9
[21] Tegg L, Cusikelney D and Keast V J 2017 Mater. Res. Express 4 065703
[22] Tegg L, Cusikelney D and Keast V J 2018 Plasmonics 13 437–44
[23] Tegg L, Cusikelney D and Keast V J 2018 Nanotechnology 29 40LT02
[24] Wang L, Zhan J, Fan W, Cui G, Sun H, Zhou L, Zhao X and Bo T 2010 Chem. Commun. 46 8833–5
[25] Li G, Guo C, Yan M and Liu S 2016 Appl. Catalysis B 183 142–4
[26] Chiang T H, Zhou Z X and Hsu J-W 2019 J. Taiwan Inst. Chem. Eng. 95 393–404
[27] Tammasebi N and Madmoli S 2018 RSC Adv. 8 7014–21
[28] Dickens P G and Whittingham M S 1968 Q. Rev. Chem. Soc. 22 30–44
[29] Cui G, Wang W, Ma M, Xe I, Shi X, Deng N, Xin J and Tang B 2015 Nano Lett. 15 7199–203
[30] Straumanis M E 1949 J. Am. Chem. Soc. 71 679–83
[31] Kang Y, Wu X and Gao Q 2019 ACS Sustainable Chem. Eng. 7 4210–9
[32] Huang Q-S, Wei W, Sun J, Mao S and Ni B-J 2019 ACS Appl. Nano Mater. 2 3802–12
[33] Bergerhoff G and Brown I D 1987 Crystallographic Databases ed FH Allen et al (Chester, England: International Union of Crystallography)
[34] Brown B W and Banks E 1954 J. Am. Chem. Soc. 76 963–6
[35] Hill R J and Howard C J 1987 J. Appl. Cryst. 20 467–74
[36] Blaha P, Schwarz K, Madsen G K H, Kvasnicka D, Luitz J, Laskowski R, Tran F and Marks L D 2018 WIEN2k, An Augmented Plane Wave + Local Orbitals Program for Calculating Crystal Properties ed K Schwarz (Austria: Techn. Universität Wien)
[37] Shanks H R, Sidles P H and Danielson G C 1963 Nonstoichiometric Compounds ed R Ward (Washington D. C: American Chemical Society) (https://doi.org/10.1021/ba-1964-0039.ch022)
[38] Höchst H, Bringans R D and Shanks H R 1982 Phys. Rev. B 26 1702–12
[39] Wolfram T and Sutcu L 1985 Phys. Rev. B 31 7680–7
[40] Hjelm A, Granqvist C G and Wills J M 1996 Phys. Rev. B 54 2436–45
[41] Ingham B, Hendy S C, Chong S V and Tallon L G 2005 Phys. Rev. B 72 075109
[42] Raj S, Hashimoto D, Matsui H, Souma S, Sato T, Takahashi T, Sarma D D, Mahedevan P and Oishi S 2006 Phys. Rev. Lett. 96 147603
[43] Raj S et al 2007 Phys. Rev. B 75 155116
[44] Bringans R D, Höchst H and Shanks H R 1981 Phys. Rev. B 24 3481–9
[45] Granqvist C G 2000 Sol. Energy Mater. Sol. Cells 60 201–62
[46] Kielwein M, Saitki K, Roth G, Fink J, Paasch G and Eggel R G 1995 Phys. Rev. B 51 10320–35
[47] Bamberger C E and Kopp O C 1993 J. Cryst. Growth 131 473–80
[48] Arnal F, Verdier P and Vincensini P D 1969 Comptes Rendus Acad. Sci. 268 1526–9
[49] Castaign R 1960 Advances in Electronics and Electron Physics ed L Marton and C Marton (NY, USA: Academic) Ch. 4 (https://doi.org/10.1016/S0065-2539(08)60212-7)
[50] Ohno T, Sarukawa K, Tokieda K and Matsumura M 2001 J. Catal. 203 82–6
[51] Takeda H and Adachi K 2007 J. Am. Ceram. Soc. 90 4059–61
[52] Tamiguchi M and Lindsay J S 2018 Photochem. Photobiol. 94 290–327
[53] Al-Azri Z H N, Chen W-T, Chan A, Jovic V, Ina T, Idriss H and Waterhouse G J N 2015 J. Catalysis. 329 355–67