Journal of Materials Chemistry C



PAPER

View Article Online



Cite this: J. Mater. Chem. C, 2024, 12, 13665

Deciphering the carrier dynamics enhancement in WO₃-containing composites: an ultrafast transient reflectance investigation†

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In recent years, the quest for WO₃-based composites with expanded optical absorption and elevated photocatalytic and photoelectrochemical performance has intensified. Despite these pursuits, a clear mechanistic understanding of the efficiency gains has been a missing piece, hindering further optimization. This study uses the transient reflectance (TR) technique to probe the intricacies of carrier dynamics in WO₃, Li_{0.1}WO₃, and the FeOOH/Li_{0.1}WO₃ composite, and found that under near-ultraviolet (NUV) illumination, the FeOOH/Li_{0.1}WO₃ system demonstrates a photo-carrier lifetime that is approximately twofold and tenfold longer than that of Li_{0.1}WO₃ and WO₃, respectively. Moreover, under near-infrared (NIR) irradiation, the FeOOH/Li_{0.1}WO₃ composite sustains carriers for nearly four times longer than the Li_{0.1}WO₃ counterpart. Our in-depth analysis points to the hole-filling effect from lithium intercalation and the FeOOH-mediated passivation of oxygen vacancies as the dual drivers behind the significantly extended carrier lifetimes, which favor processes such as charge separation, transfer, extraction, and storage. By employing femtosecond TR measurements to dissect the photo-carrier behavior in these systems, this study sheds light on the intrinsic mechanisms that have been obscured using traditional approaches. This work aims to contribute pivotal insights, potentially paving the way for the next generation of high-performance WO₃ composites in energy conversion technologies.

Received 7th April 2024, Accepted 23rd July 2024

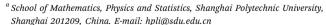
DOI: 10.1039/d4tc01430h

rsc.li/materials-c

Introduction

Tungsten oxides (WO_x, where $x \le 3$) stand as pioneers among visible light-responsive semiconductors and have long been celebrated for their exceptional attributes, including high electron mobility, remarkable electron transfer and storage capabilities, and commendable electrochemical stability - all of which are coupled with the advantage of being earth-abundant. Their potential shines

brightly in photocatalysis and photoelectrochemistry. However, the unadorned WO_r struggles with relatively low efficiency, primarily due to the swift recombination of photo-generated electrons (e⁻) and holes (h⁺). Moreover, WO_x's optical absorption is confined to the near-ultraviolet (NUV) to visible spectrum,



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[†] Electronic supplementary information (ESI) available: S1: preparation for WO₃, Li_{0.1}WO₃ and FeOOH/Li_{0.1}WO₃; S2: survey XPS spectra of the three samples; S3: transient reflectance measurements; S4: interpretation of the carrier dynamics detected using an 800 nm probe under 400 nm and an 800 nm pump for the TR measurements: S5: analysis of the carrier dynamics using the first and second order mechanisms. See DOI: https://doi.org/10.1039/d4tc01430h



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which captures only a fraction of the solar spectrum, as over half of the sun's energy lies in the near-infrared (NIR) region.

In recent years, the pursuit of WO_x-containing composites with enhanced carrier behaviors and an expanded optical absorption spectrum has seen some remarkable advancements. For example, the typical band gap of WO_r, which ranges from 2.6 to 2.8 eV, can be narrowed to approximately 0.6-0.9 eV by embedding cations such as H⁺, Li⁺, Na⁺, K⁺, and Cs⁺ into the tunneling hexagonal structured WO3, which extends the absorption spectrum from NUV to NIR.2-4 Furthermore, coupling WO_x with other semiconductors like C₃N₄, BiVO₄, and FeOOH has been shown to significantly enhance the charge carrier separation efficiency, which in turn boosts electron transfer and storage capacities.3,5-8 The broadening of the absorption spectrum is attributed to the formation of a new valence band, which is supplied by the partially occupied 5d orbitals of W⁵⁺ ions.² Despite these strides, a comprehensive understanding of the mechanisms that enhance carrier dynamics remains obscured, thereby hindering further optimization of material performance.

Traditionally, time-resolved photoluminescence (TRPL) has been the technique of choice for probing photo-carrier dynamics in photocatalytic (PC)/photoelectrochemical (PEC) systems. 9-11 However, TRPL faces limitations when it comes to examining the NIR region, where low photoluminescence quantum yields pose a challenge for detection. 12 Furthermore, the complexity of PC/PEC processes, which involve a cascade of interrelated carrier reactions such as generation, transfer, hole filling, trapping, and recombination, complicates the picture. While TRPL is a powerful tool for studying slower dynamics like carrier trapping and recombination, it may introduce significant uncertainties when measuring ultrafast carrier dynamics on the order of picoseconds, such as hole filling. 10,12

In this study, we introduce transient reflectance (TR) spectroscopy with femtosecond time resolution to elucidate the carrier dynamics in PC/PEC systems. This technique has allowed us to capture the behavior of photo-carriers in Li_{0.1}WO₃ with broadened optical absorption, and FeOOH/ Li_{0.1}WO₃ with superior PC/PEC performance, 8,13,14 using pristine WO3 as the control. Our TR findings reveal that under 400 nm illumination, photo-carriers in FeOOH/Li_{0.1}WO₃ endure more than twice as long as those in Li_{0.1}WO₃ and ten times longer than those in WO₃. Under 800 nm illumination, the FeOOH/Li_{0.1}WO₃ composite sustains photo-carriers nearly four times longer than the Li_{0.1}WO₃ alone. Further analysis indicates that the significantly extended carrier lifetimes in FeOOH/Li_{0.1}WO₃, which favor processes such as charge separation, transfer, extraction, and storage, could be attributed to the hole-filling effect from lithium intercalation and the passivation of oxygen vacancy defects by FeOOH. By delving into the factors influencing photo-carrier behavior in these sunlight harvesting systems using femtosecond TR measurements, this study aims to offer novel insights into the intrinsic mechanisms that may have been elusive using conventional methods.

Experiments and results

Static characterizations

WO₃ and Li_{0.1}WO₃ were synthesized via an in situ solvothermal approach, while the FeOOH/Li_{0.1}WO₃ composite was fabricated by depositing FeOOH onto the surface of Li_{0.1}WO₃ nanorods. Detailed procedures for sample preparation are delineated in the ESI,† S1. Conventionally, WO₃ synthesized using this method adopts an orthorhombic crystal structure. However, the incorporation of lithium through intercalation provides both Li_{0.1}WO₃ and FeOOH/Li_{0.1}WO₃ with a pure hexagonal phase of WO₃, ^{2,3,15,16} in accordance with the joint committee on powder diffraction standards (JCPDS) reference 33-1387. This phase purity is corroborated by the X-ray diffraction (XRD, ARL Equinox 3500) patterns presented in Fig. 1a. It is noteworthy that, due to the amorphous nature of FeOOH in the FeOOH/Li_{0.1}WO₃ composite, no distinct diffraction signals attributable to FeOOH were detected in the XRD analysis.

The inset of Fig. 1b presents the absorption spectra for the trio of samples, as measured using a UV-vis-NIR spectrophotometer (Lambda 950, PerkinElmer, UK). To elucidate the energy structural properties, a detailed analysis of the absorption spectra was conducted employing the Tauc equation, represented as $(\alpha h\nu)^n = B(h\nu - E_g)^{17}$, where α signifies the absorption coefficient, hv denotes the photon energy, B is a proportionality constant, $E_{\rm g}$ is the band gap energy, and n equals 1/2 for an indirect-bandgap semiconductor, as depicted in Fig. 1b. The optical data reveal that all samples exhibit robust absorption in the NUV region, characterized by an absorption edge of approximately 2.68 eV, indicated by the green dotted line in Fig. 1b. Furthermore, Li_{0.1}WO₃ and FeOOH/Li_{0.1}WO₃ manifest an additional absorption band in the visible to near-infrared (vis-NIR) region, evidenced by a reduced band edge of approximately 0.78 eV, marked by the red

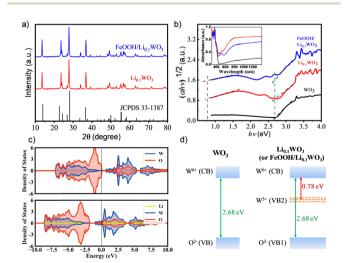


Fig. 1 (a) XRD patterns of Li_{0.1}WO₃ and FeOOH/Li_{0.1}WO₃; (b) Tauc plots of the UV-vis-NIR absorption spectra (inset) of WO₃, Li_{0.1}WO₃ and FeOOH/ $\rm Li_{0.1}WO_3$; (c) TDOS spectra of $\rm Li_{0.1}WO_3$ as well as $\rm WO_3$ for comparison; and (d) schematic diagram of the band structure of WO3 and Lio1WO3 (or FeOOH/Li_{0.1}WO₃) based on the absorption spectra.

dotted line in Fig. 1b. The former represents the intrinsic band gap energy of WO3, whereas the latter is induced by Li+ intercalation, which can be explained by the energy distribution of the density of states (DOS) derived from first-principles calculations. The DOS results depicted in Fig. 1c show that in WO₃, the 2p orbitals of O²⁻ are fully occupied, and the 5d orbitals of W6+ are vacant, constituting the valence band (VB, also noted as VB1 for Li_{0.1}WO₃ and FeOOH/Li_{0.1}WO₃ for distinguishing from VB2) and the conduction band (CB), respectively, as illustrated in the left panel of Fig. 1d.^{2,18} When lithium is incorporated to form $Li_{0.1}WO_3$, the Fermi level (E_f) shifts upward towards the CB, as compared to the pristine WO₃. Moreover, nearly all lithium metal atoms contribute to the upper CB, indicating that they are effectively ionized, thereby providing a substantial supply of free electrons. As a result, the originally vacant 5d orbitals of W6+ become partially filled, leading to the formation of W⁵⁺. These partially filled 5d orbitals of W⁵⁺ create a new valence band (VB2) positioned below the CB, which accounts for the visible to near-infrared (vis-NIR) absorption, as shown in the right panel of Fig. 1d. Additionally, as shown in Fig. 1a, the absorption spectra of Li_{0.1}WO₃ and FeOOH/Li_{0.1}WO₃ are strikingly similar, both differing from that of FeOOH.¹⁹ This similarity suggests that FeOOH/Li_{0.1}WO₃ shares a comparable spectroscopic mechanism with Li_{0.1}WO₃, and the incorporation of FeOOH has minimal impact on the primary energy structure of the latter.

The interpretation of the optical characteristics is corroborated by X-ray photoelectron spectroscopy (XPS, Thermo Scientific ESXCALAB Xi+) analysis. Fig. S1 in the ESI,† S2 displays the survey XPS spectra for the three samples. The spectra reveal not only the ubiquitous presence of W and O elements but also the distinct presence of Li and Fe, confirming the successful incorporation of Li and FeOOH into Li_{0.1}WO₃ and FeOOH/ Li_{0.1}WO₃, respectively. The Li 1s XPS spectrum for Li_{0.1}WO₃, as shown in Fig. 2a, is deconvoluted into two peaks: a principal peak at 56.3 eV and a shoulder peak at 58.1 eV. The latter is indicative of the interaction between Li and the lattice oxygen in Li_{0.1}WO₃, while the former is attributed to Li⁺ ions within the hexagonal tunnels of WO₃, ^{20,21} consistent with the DOS calculations suggesting complete ionization of lithium atoms in Li_{0.1}WO₃.

Additionally, the induced presence of W5+ ions, a consequence of Li⁺ intercalation, is detectable. Fig. 2b-d illustrate that the W 4f spectra for all three samples can be decomposed into two doublets: one for W⁶⁺ at 35.5 and 37.6 eV, and another for W5+ at 34.3 and 36.4 eV, respectively, indicating the presence of W5+ ions in each sample. In WO3, the W5+ ion peak area ratio of 3.15% is likely due to oxygen vacancy (OV) defects.²² In Li_{0.1}WO₃, this ratio increases almost twofold to 5.26%, which can be attributed to lithium intercalation and is further explained as follows: In the hexagonal Li_{0.1}WO₃ crystal structure, with uniformly dispersed trigonal and hexagonal tunnels, the intracrystalline hexagonal tunnels exhibit a high affinity for Li⁺ ions, which can be represented by the equation $WO_3 + Li^+ + e^- \rightleftharpoons [WO_3^-Li^+]^{2,3,15}$ This process allows for the introduction of a significant number of Li⁺ ions, leading to the

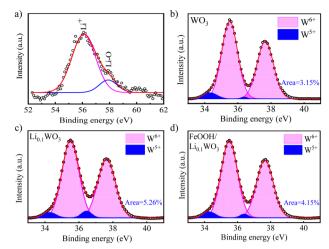


Fig. 2 (a) Li 1s XPS spectrum of Li_{0.1}WO₃ and W 4f XPS spectra of (b) WO₃, (c) Li_{0.1}WO₃ and (d) FeOOH/Li_{0.1}WO₃.

reduction of a substantial amount of W⁶⁺ to W⁵⁺ to maintain the charge balance, thereby increasing the W⁵⁺ ratio in Li_{0.1} WO₃ compared to WO₃. When Li_{0.1}WO₃ is combined with FeOOH, the W⁵⁺ ratio decreases to 4.15%. Prior research has indicated that the amorphous FeOOH layer may partially passivate OVs in the material.²³ The reduction in the W⁵⁺ ratio in FeOOH/Li_{0.1}WO₃ is likely due to the depopulation of OVs passivated by FeOOH.

Ultrafast transient reflectance (TR) measurements and data analysis

As previously outlined, the loading of FeOOH has a negligible effect on the energy structure of Li_{0.1}WO₃. Therefore, the dynamic spectral features of FeOOH/Li_{0.1}WO₃, detailed in the subsequent discussion, are primarily ascribed to the photocarriers originating from Li_{0.1}WO₃ rather than FeOOH. In the TR measurements, two distinct pump wavelengths were employed: a 400 nm wavelength to provide insights into the photo-carrier dynamics across all samples under visible light irradiation, and an 800 nm wavelength to explore those of Li_{0.1}WO₃ and FeOOH/Li_{0.1}WO₃ under NIR irradiation. Meanwhile, an 800 nm wavelength was consistently utilized as the probe regardless of which pump is used. Additional specifics of the TR experimental setup are elaborated in the ESI,† S3.

Fig. 3 and 4 display the TR measurement results for the 400 nm and 800 nm excitations, respectively. Following 400 nm excitation, Fig. 3 indicates that the three samples respond differently to the 800 nm probe. Specifically, WO3 shows a decrease in reflectance at 800 nm, while Li_{0.1}WO₃ and FeOOH/ Li_{0.1}WO₃ exhibit an opposite trend. This variation in response is likely due to the distinct band structure distributions of the materials, as further discussed in the ESI,† S4. It is recommended that, while different samples may exhibit varied responses to the 800 nm probe, the probe should consistently capture the dynamics of photo-carriers within the CBs of all samples.

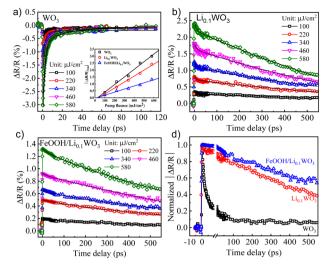


Fig. 3 (a)-(c) The pump fluence dependent TR kinetics for WO₃, Li_{0.1}WO₃ and FeOOH/Li_{0.1}WO₃ under 400 nm illumination, respectively. (d) The normalized TR traces for three samples at a pump fluence of 340 μJ cm⁻². Inset of (a): plots of $(\Delta R_t/R)_{max}$ as a function of pump fluence. Black solid curves in (a)-(c) are fitting curves using eqn (1) for the extraction of the depopulation rate constants k_1 and k_2 .

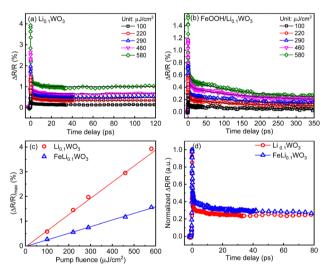


Fig. 4 (a) and (b) The pump fluence dependent TR kinetics for Li_{0.1}WO₃ and FeOOH/Li_{0.1}WO₃ under 800 nm illumination, respectively; (c) plots of $(\Delta R_t/R)_{\text{max}}$ as a function of pump fluence; (d) normalized TR traces for two samples at a pump fluence of 220 μJ cm⁻². Black solid curves on (a) and (b) are fitting curves using eqn (1) for the extraction of the depopulation rate constants k_1 and k_1 .

The dynamics triggered by 400 nm excitation primarily involve two processes: a rapid change in reflectivity to the maximum $(\Delta R_t/R)_{max}$ within the first picosecond, and a slower recovery process that extends over tens to hundreds of picoseconds. The former is typically assigned to the photo-induced e⁻/h⁺ assemblage on the CB/VB right after the photon illumination, while the latter should be linked to the relaxation of these photo-carriers through mechanisms like defect trapping and electron-hole recombination.²⁴ Obviously, photo-carriers in

WO3 relax much more quickly than those in Li0,1WO3 and FeOOH/Li_{0.1}WO₃, as illustrated in Fig. 3d. For the 800 nm excitation, except for the above two processes, an additional quick recovery process of less than 2 ps is observed. Considering that the photon energy of 800 nm (1.55 eV) is much larger than the band gap (0.78 eV) traversed, the initially excited carriers should carry much excess energy. The above quick recovery should be the dissipation process of the excess energy through phonon radiation.25 These carrier assemblage and excess energy dissipation processes are normal and have been well-documented in many semiconductors and insulators, 26,27 thus they will not be further discussed here. In the following, we aim to interpret the complex slow recovery process on a time scale to uncover the underlying mechanisms that boost the superior PC/PEC performances of these materials.

As is known to all, when materials are illuminated by photons with energy exceeding the band gap, electrons will be excited from the VB to assemble on the CB. The concentration of these excited electrons assembled on the CB, denoted as n_0 , can be determined using the formula $n_0 = Fa/hv$, where F represents the incident photon fluence, α is the material's absorption coefficient at the pump wavelength, and hv corresponds to the pump photon energy. As illustrated in the inset of Fig. 3a and c, under both 400 nm and 800 nm excitation, the maximum relative change in reflectivity, $|\Delta R_t/R|_{max}$, scales linearly with the pump fluence F (or equivalently, n_0) for all samples which leads to the connection as $\Delta R_t / R_{\text{max}} = b n_0$ with a linear coefficient b. We further hypothesize that the transient reflectivity change $\Delta R_t/R$ and the transient electron density n_t are governed by the same recovery function f(t), such that $\Delta R_t/R = |\Delta R_t/R|_{\text{max}} f(t) = b n_0 f(t) = b n_t$. Therefore, the observed slow recovery is indicative of the electron depopulation process within the probed volume.

In semiconductors, the depopulation photo-carriers is typically described by the rate equation $-dn_t/dt = k_1n_t + k_2n_t^2 +$ $k_3 n_t^{3}$, ^{25,28} where the terms on the right-hand side correspond to: (1) first-order trap state-mediated recombination; (2) second-order non-geminate or free carrier recombination; and (3) three-body Auger recombination.²⁹ Here, k_1 , k_2 and k_3 are the respective depopulation rate constants. Given the low pump fluence $(100-580 \,\mu\text{J cm}^{-2})$ used in this study, Auger recombination can be disregarded. Consequently, the rate equation simplifies to $-dn_t/dt = k_1n_t + k_2n_t^2$, whose analytic solution is given by

$$n_{t} = k_{1}n_{0}/[(k_{2}n_{0} + k_{1})e^{k_{1}t} - k_{2}n_{0}].$$
 (1)

By fitting the recovery processes of the three samples with eqn (1), as depicted by the solid black curves in Fig. 3a-c and 4a and b, the corresponding depopulation rate constants k_1 and k_2 can be extracted. For all the samples, the fluctuation of the extracted constants across different pump fluences is minimal; thus, an average value from all fluences ranging from 100 to 580 μ J cm⁻² is used for the discussion, as listed in Table 1. By calculating $k_2 \times n_0$ (Table 1) and comparing it with k_1 , we found that the former is consistently two or three orders of magnitude

Table 1 k_1 and k_2 for WO₃, Li_{0.1}WO₃ and FeOOH/Li_{0.1}WO₃ under 400 nm and 800 nm excitation. n_0 is calculated using $n_0 = F\alpha/h\nu$ with $F = 330 \mu J \text{ cm}^{-2}$ (an average value of the used five pump fluences) and the measured $\alpha = 2.0 \times 10^4$ cm⁻¹, 2.0×10^4 cm⁻¹ and 1.8×10^4 cm⁻¹ at 400 nm for WO3, Li_{0.1}WO3 and FeOOH/Li_{0.1}WO3, and α = 2.2 \times $10^4~cm^{-1}$ and 1.2×10^4 cm⁻¹ at 800 nm for Li_{0.1}WO₃ and FeOOH/Li_{0.1}WO₃, respectively

Pump wavelength	Sample	$_{\left(\times10^{9}\text{ s}^{-1}\right)}^{k_{1}}$	$(\times 10^{-12} \text{ cm}^3 \text{ s}^{-1})$	$\begin{array}{c} k_2 \times n_0 \\ (\times 10^7 \text{ s}^{-1}) \end{array}$
400 nm	WO_3	4.00	6.32	8.40
	$Li_{0.1}WO_3$	0.65	0.88	1.17
	FeOOH/Li _{0.1} WO ₃	0.36	0.39	0.47
800 nm	$Li_{0.1}WO_3$	9.75	38.3	99.0
	$FeOOH/Li_{0.1}WO_{3}$	2.16	9.00	13.0

smaller than the later. According to eqn (1), this suggests that the contribution of the second-order mechanisms is significantly weaker. In other words, the electron depopulation processes are predominantly governed by the first-order trap state-mediated recombination. This conclusion is further supported by a more detailed analysis provided in the ESI,† S5. Consequently, the subsequent discussion will primarily focus on the first-order mechanism, as characterized by k_1 , for further analysis.

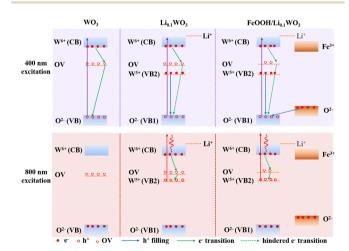
As detailed in Table 1, the depopulation rate constant k_1 exhibits a pronounced sample-dependent behavior under both 400 nm and 800 nm excitation. Specifically, under 400 nm excitation, the value of k_1 for WO₃ is observed to be 4.00×10^9 s⁻¹, which diminishes to $0.65 \times 10^9 \text{ s}^{-1}$ for $\text{Li}_{0.1}\text{WO}_3$ and further to $0.36 \times 10^9 \text{ s}^{-1}$ for FeOOH/Li_{0.1}WO₃, reflecting a reduction by factors of 6 and 10, respectively. Meanwhile, under 800 nm excitation, k1 for Li_{0.1}WO₃ is approximately $9.75 \times 10^9 \text{ s}^{-1}$, which declines to approximately $2.16 \times 10^9 \text{ s}^{-1}$ for FeOOH/Li_{0.1}WO₃, indicating a reduction by a factor of 4. According to eqn (1), a lower k_1 signifies a slower electron depopulation rate, which in turn implies a longer electron lifetime, and vice versa. Consequently, the dynamic measurements suggest that the electron lifetime in FeOOH/Li_{0.1}WO₃ is extended compared to that in Li_{0.1}WO₃, and both are substantially longer than the lifetime observed in pure WO₃.

Discussion

Notably, TR measurements indicate that under 400 nm excitation, the electron lifetime in the FeOOH/Li_{0.1}WO₃ composite is approximately twice that in Li_{0.1}WO₃ and nearly tenfold that in WO₃. Meanwhile, under 800 nm excitation, the electron lifetime in FeOOH/Li_{0.1}WO₃ is roughly four times longer than in Li_{0.1}WO₃, as detailed in Table 1. We now explore the potential mechanisms that contribute to the extended carrier lifetimes observed in these samples. Firstly, we consider the behavior of charge carriers under 400 nm excitation. Typically, WO₃ possesses a band gap of 2.68 eV, characterized by the filled 2p orbitals of O²⁻ constituting the VB and the unoccupied 5d orbitals of W⁶⁺ forming the CB, as depicted in Fig. 1d and Scheme 1. Concurrently, as previously noted, the synthesis of WO₃ invariably introduces OVs, which create trap states, illustrated as OV in Scheme 1. Prior density functional theory (DFT) calculations have indicated that in WO3, minor intrinsic OV

defects are more likely to be dispersed rather than aggregated. Furthermore, the trap states arising from these isolated OVs are anticipated to be situated 0.48 to 0.62 eV below the conduction band edge, 30 which aligns with the prevalent perspective that OVs in WO₃ act as shallow electron donors. ^{31,32} Upon exposure to 400 nm (3.10 eV) photons, electrons from the VB of WO₃, as well as those in Li_{0.1}WO₃ and FeOOH/Li_{0.1}WO₃, are excited to the CB, leaving behind holes on the VB. Given the indirect bandgap nature of WO3, the direct relaxation of these excited electrons back to the VB is challenging.29 Consequently, these electrons are typically captured by OVs temporarily before returning to the VB to recombine with holes, as indicated by the green arrows in the WO₃ panel of Scheme 1 for 400 nm excitation. It is widely understood that the initial trapping process is of the first order, whereas the recombination process is of the second order. The TR data for WO3 confirm that the recovery processes are predominantly governed by the firstorder mechanism, suggesting that these are indeed the trapping events of electrons by OVs.

When considering Li_{0.1}WO₃, as described above, the intercalation of lithium atoms leads to the reduction of some W⁶⁺ ions to W⁵⁺. Consequently, in addition to the intrinsic CB and VB (denoted as VB1 in Li_{0.1}WO₃ and FeOOH/Li_{0.1}WO₃) of WO₃, the partially occupied 5d orbitals of W5+ constitute a new valence band, referred to as VB2 in Scheme 1. This results in a reduced band gap of approximately 0.78 eV.² Considering that lithium intercalation exerts negligible influence on the intrinsic band gap of WO₃, it is reasonable to expect that the positioning of OV states in Li_{0.1}WO₃ would closely mirror that in WO₃. Accordingly, as illustrated in Scheme 1, VB2 is anticipated to be positioned marginally lower than the OV states. For Li_{0.1}WO₃ right after the 400 nm illumination, there should be abundant excited e⁻/h⁺ on CB/VB1. However, electrons occupying VB2 are likely to swiftly transfer to VB1 to neutralize h⁺ (sketched as the blue arrow in Scheme 1 on the Li_{0.1}WO₃ panel of 400 nm excitation). This hole filling behavior, which has been observed intensively in semiconductors,24 leads to a reduction in h+



Scheme 1 Schematic diagram of hindered photo-carrier recombination in $Li_{0.1}WO_3$ and $FeOOH/Li_{0.1}WO_3$ under 400 nm and 800 nm irradiation.

concentration on VB1, impeding the migration of electrons trapped at OVs to VB1 ((sketched as the green dotted arrow in Scheme 1 on the Li_{0.1}WO₃ panel of 400 nm excitation)). Consequently, the transition of electrons from the CB to OV is obstructed, and e remain in the CB for an extended duration, elucidating the observed prevalence of prolonged first-order relaxation processes in Li_{0.1}WO₃ as compared to WO₃.

Upon the deposition of FeOOH onto Li_{0.1}WO₃, while the energy level structure remains largely unaltered, OVs in Li_{0.1}WO₃ are partially passivated as evidenced by the aforementioned XPS data analysis. Consequently, the trapping effect of OVs on e is diminished. Meanwhile, FeOOH possesses an intrinsic band gap of approximately 2.2 eV, which is marginally smaller than that of WO₃.³³ When integrated with Li_{0.1}WO₃, the VB of FeOOH, which is also derived from the 2p orbitals of O^{2-} , is anticipated to be marginally higher in energy than that of Li_{0.1}WO₃, as depicted in Scheme 1. In this case, for FeOOH/ Li_{0.1}WO₃ illuminated by 400 nm photons, in addition to the hole filling from VB2 to VB1 (vertical blue arrow in Scheme 1 on the FeOOH/Li_{0.1}WO₃ panel of 400 nm excitation), holes on the VB1 are also neutralized by electrons from the 2p orbitals of O²⁻ in FeOOH (oblique blue arrow in Scheme 1 on the FeOOH/ Li_{0.1}WO₃ panel of 400 nm excitation). The combined effect of the reduced OV trapping and the enhanced hole filling is expected to decelerate electron relaxation, thereby rationalizing the extended carrier lifetime observed in the FeOOH/Li_{0.1}WO₃ composite compared to Li_{0.1}WO₃ alone.

Secondly, we discuss the behavior of charge carriers under 800 nm excitation. Given the weak absorbance of WO3 in the NIR region, no effective TR data were obtained for this material. Therefore, our analysis in this section will focus solely on Li_{0.1}WO₃ and FeOOH/Li_{0.1}WO₃. As previously mentioned, Li_{0.1}WO₃ and FeOOH/Li_{0.1}WO₃ exhibit two distinct bandgaps, 2.68 eV and 0.78 eV, respectively. Upon 800 nm irradiation, the photon energy of 1.55 eV, being lower than the intrinsic band gap of 2.68 eV, will only excite electrons from VB2, leading to the formation of hot electrons and holes on the CB and VB2. Once cooled to the bottom of the CB, electrons are initially captured by OVs before recombining with holes in VB2 (as depicted by the green arrows in Scheme 1 for the 800 nm excitation of both Li_{0.1}WO₃ and FeOOH/Li_{0.1}WO₃). As previously discussed, the OVs in FeOOH/Li_{0.1}WO₃ may be partially passivated by the FeOOH component. Therefore, in FeOOH/ Li_{0.1}WO₃, the trapping of electrons is obstructed, resulting in an extended residence time for electrons in the CB relative to $Li_{0.1}WO_3$.

The prolonged electron lifetime should have a positive effect to the PC/PEC efficiencies, which can be interpreted with an example of the photocatalytic process of CH₄ and H₂O₂ reacting to produce CH₃OH. This process can be succinctly summarized as follows: Firstly, when the incident light energy hv is not less than the band gap width E_g , electrons in the valence band absorb the light energy and transition to the CB, while simultaneously creating holes in the VB. Secondly, the generated e and h⁺ migrate to the semiconductor surface under the influence of the electric field or diffusion; finally, the electrons with

reducing power react with H₂O₂ to form hydroxyl radicals, which then react with CH₄ to produce CH₃OH. In this process, to achieve a higher catalytic efficiency, it is necessary to ensure that the photo-generated electrons effectively separate from the photo-generated holes without recombination and successfully migrate to the semiconductor surface. In this study, the TR technique directly observes the lifetime of photo-generated electrons. For example, TR experiments observed a longer lifetime of photo-generated electrons in FeOOH/Li_{0.1}WO₃, which on one hand proves that they are effectively separated from the photo-generated holes without recombination, and on the other hand, the longer survival time also provides ampler time for the photo-generated electrons to transfer to the semiconductor surface. This is in accordance with the greatly improved photocatalytic efficiency of FeOOH/Li_{0.1}WO₃ compared with Li_{0.1}WO₃ and WO₃ observed previously.³

Except for the elevated photocatalytic efficiency, WO₃-based composites have been proved to demonstrate significant enhancements in PEC properties. For instance, A_rWO₃ (where A represents H⁺, Na⁺, K⁺) not only broadens the optical absorption spectrum to the NIR region but also displays notably enhanced photoelectric anticorrosion capabilities; in addition, under simulated sunlight irradiation, the heterostructured WO₃/FeOOH photoanode has been observed to deliver a photocurrent density nearly double that of pristine WO3.8 Given the importance of prolonged carrier lifetimes in boosting charge transfer, separation, extraction, and storage efficiencies within sunlight harvesting systems, we propose that the superior PEC performances of these composites may also be partially attributed to the presence of long-lived photo-carriers in them.

Conclusions

In this study, the TR technique was employed to scrutinize the dynamics of photo-carriers within WO3-containing composites, specifically Li_{0.1}WO₃ and FeOOH/Li_{0.1}WO₃, in comparison to pure WO3. The experimental findings indicate that under 400 nm excitation, the photo-carriers in FeOOH/Li_{0.1}WO₃ exhibit a significantly extended lifetime, enduring approximately twofold and tenfold longer than those in Li_{0.1}WO₃ and pure WO₃, respectively. Furthermore, under 800 nm excitation, the photo-carriers in FeOOH/Li_{0.1}WO₃ demonstrate a lifetime nearly four times longer than those in Li_{0.1}WO₃. These prolonged lifetimes are posited to enhance the PC/PEC performance, which can be ascribed to the hole filling effect arising from lithium intercalation and the passivation mechanism of OV defects by FeOOH. This investigation not only offers valuable insights for optimizing the PC/PEC performance of WO3-based systems but also introduces innovative perspectives on the underlying mechanisms that may elude traditional investigative approaches.

Author contributions

Investigation, data analysis and writing - original draft: H. Z.; DFT calculations: T. J.; XPS measurement and data analysis: M. Z.; sample preparation: H. L.; resources, project administration, and supervision: F. L. All authors discussed the results and contributed to the final manuscript.

Data availability

The data that support the findings of this study are available from the corresponding author, H. Z., upon reasonable request.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported by the Foundation for University Young Teacher by Shanghai Municipal Education Commission under Grant No. ZZ202215003.

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