Deciphering the carrier dynamics enhancement in WO$_3$-containing composites: an ultrafast transient reflectance investigation

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S1. Preparation for WO$_3$, Li$_{0.1}$WO$_3$ and FeOOH/Li$_{0.1}$WO$_3$

The three samples were synthesized using an in situ solvothermal method following Ref. 3. Typically, for the preparation of WO$_3$, 0.5 mmol of WCl$_6$ was dissolved in 40 mL of absolute ethanol and stirred for 40 minutes. Subsequently, 8 mL of CH$_3$COOH was added, followed by an additional 10 minutes of stirring, resulting in a homogeneous precursor solution. This solution was then transferred into a Teflon-lined stainless steel autoclave, sealed, and heated at 200 °C for 30 hours in an oven. The resulting WO$_3$ sample was collected, washed with deionized water several times, and dried at 50 °C to obtain pure WO$_3$. The synthesis of Li$_{0.1}$WO$_3$ followed a similar procedure to that of WO$_3$, with one additional step: 17 mg of LiNO$_3$ was introduced along with CH$_3$COOH during the preparation of the precursor solution.

The fabrication of FeOOH/Li$_{0.1}$WO$_3$ commenced with the dissolution of 1 mmol of FeCl$_3$·6H$_2$O in 40 mL of absolute ethanol, stirred for 5 minutes. Then, 200 mg of pre-synthesized Li$_{0.1}$WO$_3$ was added to the solution and subjected to ultrasonication for 10 minutes. Following this, 3 mmol of NH$_4$HCO$_3$ was incorporated into the mixture and stirred for 8 hours, leading to the formation of amorphous FeOOH on the surface of Li$_{0.1}$WO$_3$. Ultimately, the product was collected by centrifugation, washed with deionized water several times, and dried under vacuum at 50 °C for 6 hours to obtain the FeOOH/Li$_{0.1}$WO$_3$ composite.

S2. Survey XPS spectra of WO$_3$, Li$_{0.1}$WO$_3$ and FeOOH/Li$_{0.1}$WO$_3$
S3. Transient reflectance (TR) measurements

Transient Reflectance (TR) measurements were conducted using a 1 kHz Ti:sapphire laser system (Legend Elite HE+USP-III, Coherent, Inc.), which provides 40 fs pulses at a central wavelength of 800 nm. In the case of 800 nm pump-800 nm probe measurements, the laser output was divided into two beams by a 9:1 beam splitter, with the more intense beam designated as the pump and the less intense one as the probe. For the 400 nm pump-800 nm probe measurements, the 400 nm pump beam was generated through second harmonic generation using Type I BBO crystals. For both measurement setups, the pump spot diameter was approximately 2 mm, significantly larger than that of the probe spot at 0.2 mm, facilitating spatial overlap of the two beams. The pump fluence was adjusted from 100 to 580 μJ/cm², while the probe fluence was maintained at approximately 10 μJ/cm². The TR signal was acquired by altering the temporal interval between the pump and probe pulses, utilizing a high-precision delay stage positioned in the pump beam’s path. Throughout data acquisition, the pump beam was modulated at 220 Hz by an optical chopper, and the resultant intensity changes of the reflected probe beam were collected using the lock-in amplification technique.

S4. Interpretation of the carrier dynamics detected by 800 nm probe under 400 nm and 800 nm pump in TR measurements.

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**Fig. S1** Survey XPS spectra of WO$_3$, Li$_{0.1}$WO$_3$ and FeOOH/Li$_{0.1}$WO$_3$.

**Scheme S1.** Schematic diagram of the carrier dynamics detected by 800 nm probe under 400 nm and 800 nm pump in TR measurements.
As detailed in the main text, WO₃ possesses an intrinsic bandgap of approximately 2.68 eV, with the 2p orbitals of O²⁻ constituting the valence band (VB) and the 5d orbitals of W⁶⁺ forming the conduction band (CB). In contrast, Li₀.₁WO₃ and FeOOH/Li₀.₁WO₃ exhibit an additional bandgap of approximately 0.78 eV due to the formation of a new valence band (VB₂ as depicted in Scheme S1) induced by lithium intercalation. Due to the varying band structure distributions of the above materials, the 800 nm wavelength probes the dynamics of carriers on different bands across them, as discussed in the following.

For clarity, we will explore this subject across three distinct scenarios: Case I involves WO₃ being pumped at 400 nm and probed at 800 nm; Case II pertains to Li₀.₁WO₃ (or FeOOH/Li₀.₁WO₃) being pumped at 400 nm and probed at 800 nm; Case III examines Li₀.₁WO₃ (or FeOOH/Li₀.₁WO₃) when both pumped and probed at 800 nm.

In Case I, 400 nm photons, with an energy of 3.10 eV that surpasses the 2.68 eV bandgap of WO₃, are anticipated to induce a transition from the O²⁻ 2p to the W⁶⁺ 5d levels (as depicted by thick purple arrows in Scheme S1 on the WO₃ panel). Here, the 800 nm photons are capable of directly monitoring the dynamics of photo-excited electrons in the CB (illustrated by thin red arrows in Scheme S1 on the WO₃ panel), given that their photon energies are insufficient to bridge the 2.68 eV bandgap.

For Case II, although the 400 nm photons stimulate an O²⁻ 2p to W⁶⁺ 5d transition in Li₀.₁WO₃ and FeOOH/Li₀.₁WO₃, akin to WO₃ (as indicated by thick purple arrows in Scheme S1 on the respective panels), the 800 nm wavelength primarily investigates the carrier dynamics on the VB₂ level (illustrated as thin red arrows in Scheme S1 on the Li₀.₁WO₃ and FeOOH/Li₀.₁WO₃ panel), which lies 0.78 eV (or less than 1.55 eV) below the CB. The rationale is that electrons initially present in VB₂, which are greatly outnumbered the photo-excited electrons in the CB, are more responsive to the probing photons. It should be noted that, with a 400 nm pump, both transitions from O²⁻ 2p to W⁶⁺ 5d and from W⁵⁺ 5d to W⁶⁺ 5d can be excited. However, considering that in the Li₀.₁WO₃ and FeOOH/Li₀.₁WO₃ samples used in this study, lithium is added in very small quantities, the number of electrons on W⁵⁺ 5d is significantly lower than those on O²⁻ 2p. Consequently, the 400 nm photons will be preferentially absorbed by the electrons on O²⁻ 2p.

This interpretation is supported by the differential reflectance changes observed in Fig. 3 for WO₃ and Li₀.₁WO₃ (or FeOOH/Li₀.₁WO₃). Promptly following the 400 nm excitation, which triggers the same O²⁻ 2p to W⁶⁺ 5d transition across all samples, WO₃’s reflectance at 800 nm diminishes, while that of Li₀.₁WO₃ and FeOOH/Li₀.₁WO₃ escalates. This phenomenon can be clarified as follows: after the 400 nm excitation, photo-electrons amass in the CB. For WO₃, which is naturally unresponsive to 800 nm light, this accumulation leads to heightened absorption at 800 nm and a subsequent drop in reflectance. Conversely, in Li₀.₁WO₃ and FeOOH/Li₀.₁WO₃, the electron aggregation in the
CB might reduce the likelihood of VB2 to CB transitions, resulting in diminished absorption and an increase in reflectance at 800 nm.

In Case III, 800 nm photons, with their energy of 1.55 eV that is below the 2.68 eV threshold but above the 0.78 eV mark, are expected to catalyze a transition from $W^{5+} 5d$ to $W^{6+} 5d$ in Li$_{0.1}$WO$_3$ and FeOOH/Li$_{0.1}$WO$_3$ (as shown by the thick red arrow in Scheme S1 on the respective panels). Here, the 800 nm wavelength is also anticipated to scrutinize the carrier dynamics on VB2, in a manner analogous to Case II. This assignment is corroborated by the similar responses of Li$_{0.1}$WO$_3$ and FeOOH/Li$_{0.1}$WO$_3$ to the 800 nm probe under both 400 nm and 800 nm excitations. Li$_{0.1}$WO$_3$ and FeOOH/Li$_{0.1}$WO$_3$ increases. Same as described for Case II, this increase can be ascribed to the electron accumulation in the CB, which lowers the probability of VB2 to CB transitions, thereby reducing absorption and increasing reflectance at 800 nm.

Above all, it is crucial to recognize that for WO$_3$, the 800 nm wavelength exclusively monitors the dynamics of photo-electrons in the CB, which is a straightforward process. Whereas for Li$_{0.1}$WO$_3$ and FeOOH/Li$_{0.1}$WO$_3$, the dynamics of VB2 electrons fundamentally stem from the behaviors of photo-excited electrons in the CB. Consequently, under either pump condition, the reflectance variation at 800 nm also mirrors the electron dynamics in the CB.

S5. Analysis of carrier dynamics participated by the first and second order mechanisms

As depicted in the inset of Fig. 3a and in Fig. 4c within the main text, the maximum relative transient reflectance change, denoted as \( \left( \frac{\Delta R}{R} \right)_{\text{max}} \), exhibits a linear dependence on the pump fluence, \( F \). This relationship takes into account the initial excited carrier density, \( n_0 \), which is formulated as \( n_0 = \frac{F \alpha}{h \nu} \), where \( \alpha \) represents the sample's absorption coefficient at the pump wavelength, and \( h\nu \) signifies the pump photon energy. Consequently, \( \left( \frac{\Delta R}{R} \right)_{\text{max}} \) can be articulated as a function of \( n_0 \):

\[
\left( \frac{\Delta R}{R} \right)_{\text{max}} = B n_0.
\]

Assuming that the change in transient reflectance, \( \Delta R_t/R \), and the transient photo-electron density, \( n_t \), share an identical recovery function, \( f(t) \), the equation evolves to

\[
\frac{\Delta R_t}{R} = \left( \frac{\Delta R}{R} \right)_{\text{max}} \cdot f(t) = b n_0 \cdot f(t) = b n_t.
\]

This formulation implies that the observed slow recovery actually corresponds to the depopulation process of photo-electrons within the probed volume.

The depopulation process of photo-carriers in semiconductors is typically characterized by a straightforward rate equation:

\[
-\frac{dn_t}{dt} = k_1 n_t + k_2 n_t^2 + k_3 n_t^3.
\]  

(1)

The terms on the right-hand side are ascribed to: (1) first-order trap state-mediated recombination or carrier diffusion; (2) second-order non-geminate recombination; and (3) third-order Auger
recombination, with $k_1$, $k_2$, and $k_3$ being the respective depopulation rate constants. Given the low pump fluence (100-580 \( \mu \text{J/cm}^2 \)) utilized in this study, the contribution of the third-order process is considered negligible.

To deepen the comprehension of these dynamics, a preliminary analysis of the experimental data was conducted under the assumption that the recovery process could be predominantly governed by either the first or second-order terms. If the first-order mechanism prevails, Equation (1) simplifies to

$$\frac{dn_1}{dt} = k_1n,$$

yielding $n_1 = n_1 e^{-k_1t}$. Conversely, if the second-order mechanism is dominant, the equation takes the form $n_2 = \frac{n_2}{k_2 n_2 t + 1}$. Here $n_1$ and $n_2$ represent the photo-carrier densities depopulated via the first and second-order mechanisms, respectively. Thus, if the first-order mechanism is dominant, the associated change in reflectivity follows the equation

$$\frac{\Delta R_t}{R} = b n_1 e^{-k_1 t},$$

or in logarithmic form,

$$\ln \left( \frac{\Delta R_t}{R} \right) = \ln (bn_1) - k_1 t,$$

indicating a linear dependence of $\ln \left( \frac{\Delta R_t}{R} \right)$ on time delay, $t$. Similarly, if the second-order mechanism predominates, the reflectivity change aligns with the equation

$$\frac{\Delta R_t}{R} = b \frac{n_2}{k_2 n_2 t + 1} \left( \frac{\Delta R_t}{R} \right)^{-1} = \frac{k_2}{b} + \frac{1}{bn_2},$$

signifying a linear relationship of $\frac{\Delta R_t}{R}$ with time $t$. 

![Graphs showing normalized ΔR/R vs. time delay for different fluences](image-url)
Fig. S2 Relative reflectance change normalized at \( \frac{\Delta R}{R} \) for (a) WO\(_3\), (c) Li\(_{0.1}\)WO\(_3\), and (e) FeOOH/Li\(_{0.1}\)WO\(_3\) under 400 nm pump and (b), (d), (f) the corresponding time dependences of \( \ln \left( \frac{\Delta R}{R} \right) \) during the recovery process. The solid lines in (b), (d) and (f) are linear-fittings to the experimental data presented as scattered points. The arrows indicate the rise in pump fluence.

Figs. S2b, d, and f present the time-dependent \( \ln \left( \frac{\Delta R}{R} \right) \) for WO\(_3\), Li\(_{0.1}\)WO\(_3\), and FeOOH/Li\(_{0.1}\)WO\(_3\) under 400 nm excitation, while Figs. S3b and d depict the same for Li\(_{0.1}\)WO\(_3\) and FeOOH/Li\(_{0.1}\)WO\(_3\) under 800 nm excitation. The findings indicate that the photo-carrier depopulation in all samples is predominantly governed by a first-order process.

Additionally, it is generally expected that the second-order process would accelerate with increased pump fluence. However, as demonstrated in Fig. S2a, c, e, and S3a, c, the observed depopulation processes are independent of pump fluence, further substantiating the predominance of first-order mechanisms. These outcomes are consistent with the conclusions drawn in the main text, which suggest a minimal involvement of the second-order mechanism.

Fig. S3 Relative reflectance change normalized at \( \frac{\Delta R}{R} \) for (a) Li\(_{0.1}\)WO\(_3\) and (c) FeOOH/Li\(_{0.1}\)WO\(_3\) under 800 nm pump and (b), (d) the corresponding time dependences of \( \ln \left( \frac{\Delta R}{R} \right) \) during the recovery process. The solid lines in (b) and (d) are the fitting to the experimental data presented as scattered points. The arrows indicate the rise in pump fluence.