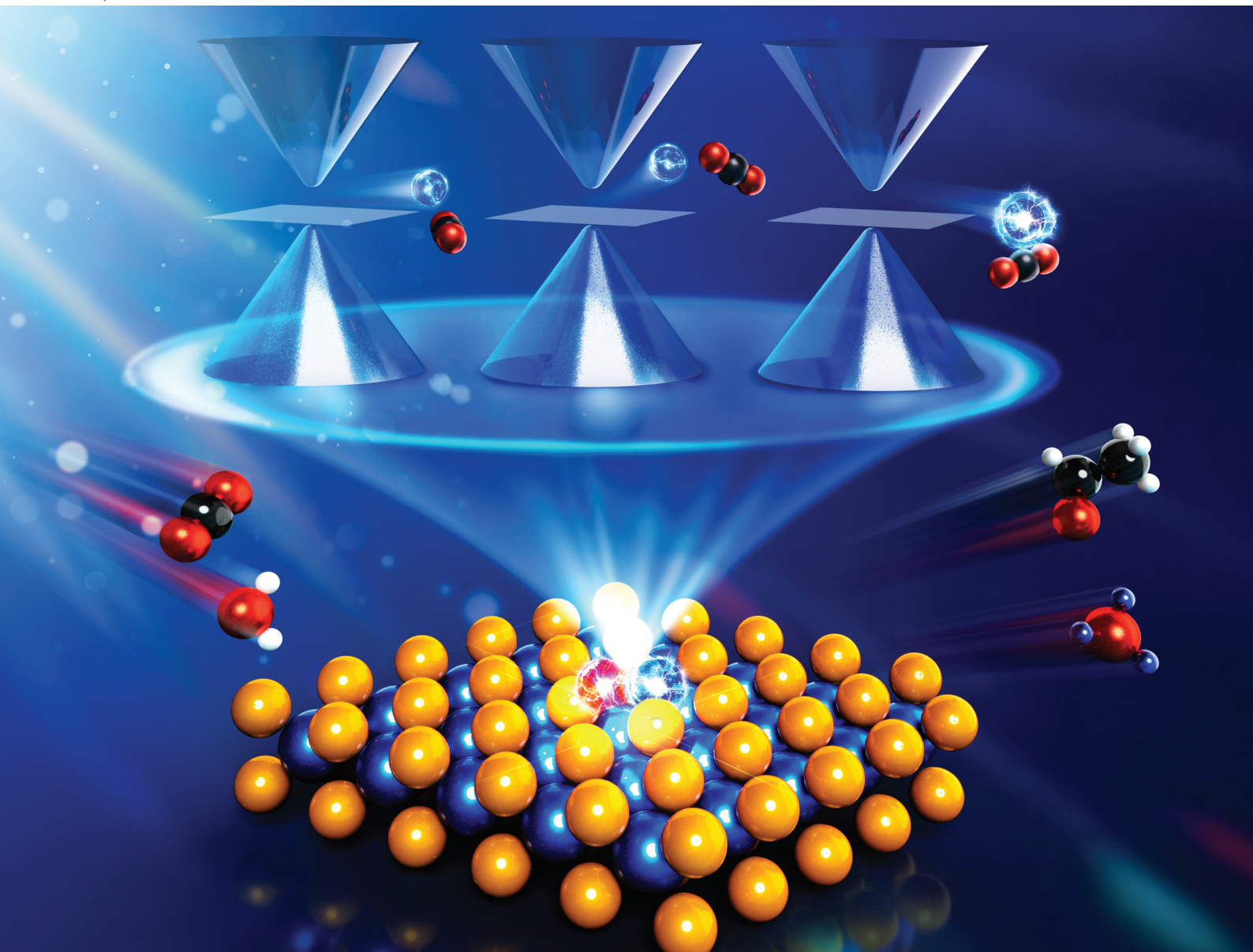


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An *operando* photoconductivity platform reveals defect–adsorbate–carrier coupling in ultrathin MoS₂ for solar-driven CO₂ reduction

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Understanding the interfacial charge dynamics between a catalyst and adsorbate is vital for advancing solar-driven CO₂ reduction. However, the mechanistic coupling between defects, surface adsorbates, and photogenerated carriers remains poorly defined under *operando* conditions, limiting rational catalyst design. Here, we introduce a high-sensitivity *in situ* photoconductivity (PC) platform to probe carrier dynamics in a 3 nm-thick MoS₂ film under simulated gas-phase CO₂ photoreduction conditions (AM1.5G illumination, CO₂/H₂O atmosphere). Prominent persistent PC (PPC) was observed under vacuum/UV irradiation, attributed to approximately 5% sulfur vacancies acting as deep-level traps (bandgap: 1.76 eV; electron capture barrier: 0.47 eV). Upon exposure to humid CO₂, the photocurrent dropped by 82%, with significantly shortened rise and decay time constants, indicating accelerated recombination *via* enhanced defect–adsorbate interactions. To explain these findings, we propose a conceptual defect–adsorbate energy alignment model describing three distinct electronic coupling scenarios, including (i) energetic alignment of defect–adsorbate states, (ii) modulation of adsorbate LUMO levels to higher energies, and (iii) lowering of adsorbate LUMO levels under specific coupling conditions. This model represents the first mechanistic framework linking adsorption, defect energetics, and charge retention in defective ultrathin 2D photocatalysts. It establishes a foundation for rational catalyst design, with future theoretical and spectroscopic validation expected to further strengthen this framework. Our *operando* PC platform offers mechanistic insights into defect–adsorbate–carrier coupling and provides a promising diagnostic tool for guiding the development of high-efficiency ultrathin 2D CO₂ catalysts.

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1. Introduction

Carbon capture, utilization, and storage (CCUS) technologies are widely regarded as critical strategies for achieving net-zero

carbon emissions.^{1–3} Among the various CO₂ utilization approaches, solar-driven gas-phase photocatalytic CO₂ reduction reactions (PCCO₂RRs) offer a promising pathway for converting CO₂ into high-value fuels and chemicals using renewable energy sources.^{4–6} However, traditional particulate photocatalysts such as metal oxides typically possess wide bandgaps, which limit light absorption and lead to long carrier diffusion paths and weak surface reactivity, consequently reducing overall catalytic performance.^{7,8} In contrast, ultrathin two-dimensional (2D) semiconductor photocatalysts, such as molybdenum disulfide (MoS₂), have emerged as attractive alternatives due to their high surface-to-volume ratios, short charge migration lengths, and tunable electronic structures.^{9–13} Their nanoscale thickness enhances charge separation and transport efficiency while reducing bulk recombination losses.^{14,15} However, the full catalytic potential of these materials remains underexplored due to an incomplete understanding of how interfacial charge dynamics and gas-phase surface reactions co-evolve under realistic operating conditions.

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Pristine MoS₂ was initially reported as an efficient HER catalyst because its edge sites are catalytically active,¹⁶ whereas the basal plane is inert and unfavorable for catalytic reactions. However, the overall surface area of MoS₂ is dominated by the basal plane rather than the edge sites. If the basal plane properties can be effectively tuned, MoS₂ could potentially be transformed from an HER catalyst into a promising material for CO₂ reduction.¹⁷ This possibility has attracted significant attention in recent years.^{17–19} Strategies such as sulfur vacancy engineering and the introduction of supported metal single atoms or nanoparticles have been demonstrated to modify the electronic structure and catalytic behavior of the basal plane.^{18,19} These approaches endow MoS₂ with remarkable potential for CO₂ conversion and have stimulated a new research direction.

Despite advances in the design and synthesis of 2D photocatalysts, the mechanistic coupling among intrinsic defects, adsorbed CO₂ molecules, and photogenerated charge carriers remains poorly understood under *operando* conditions.²⁰ A key mechanistic step involves the transfer of photogenerated electrons to adsorbed CO₂ molecules, which leads to the formation of CO₂^{•-}, a crucial intermediate in the activation process.^{8,21} The efficiency of this process depends not only on charge separation and transport but also on the energetic alignment and dynamic interaction between surface adsorbates and intrinsic defect states, which together modulate the interfacial charge landscape.^{8,21} Intrinsic defects in ultrathin 2D photocatalysts, such as sulfur vacancies (V_S) or lattice distortions, substantially affect charge carrier behavior, enhance molecular adsorption, and regulate surface reaction pathways critical to photocatalytic CO₂ conversion.^{22–24}

To evaluate catalytic performance, *ex situ* methods, such as gas chromatography (GC), gas chromatography–mass spectrometry (GC-MS), and nuclear magnetic resonance (NMR), are widely employed for product quantification,²⁵ yet these techniques provide no insight into real-time charge dynamics or surface–defect–adsorbate coupling. *In situ* spectroscopy, including X-ray photoelectron spectroscopy (XPS)^{26,27} and diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS),^{28–30} enable chemical-state analysis of adsorbed species. However, these techniques primarily provide static snapshots of surface composition rather than dynamic information on charge behavior. Ultrafast transient absorption (TA) spectroscopy addresses this limitation by tracking carrier relaxation and trapping on the picosecond timescale and has been applied to study defect effects in In₂O_{3–x}(OH)_y systems under photothermal CO₂/H₂ conditions.^{30–32} However, TA is equipment intensive, and its ultrashort temporal window limits its applicability to steady-state processes such as persistent carrier retention or defect-mediated recombination, both of which are critical for determining photocatalytic turnover. These limitations expose a critical measurement gap: the lack of *operando*-compatible, steady-state electronic diagnostics capable of continuously resolving how surface–adsorbate interactions modulate charge retention *via* defect states. Without such tools, the role of defect–adsorbate–carrier coupling in regulating activation pathways and selectivity during the PCCO₂RR remains speculative. Therefore, there is an urgent need for scalable, real-time diagnostic strategies that can directly probe

photocatalyst dynamics and their coupling with surface-adsorbed CO₂ under relevant gas-phase conditions, thus providing mechanistic guidance for rational defect engineering in ultrathin 2D photocatalysts.

Photoconductivity (PC) is a classical yet versatile optoelectronic technique that enables time-resolved monitoring of charge generation, transport, and recombination through systematic modulation of light intensity, wavelength, gas composition, and temperature under *operando* conditions.^{33–35} Compared to conventional *ex situ* methods, PC is particularly well suited for probing carrier dynamics in low-dimensional semiconductors under reactive environments. PC measurements capture illumination-induced conductivity variations, serving as indirect but sensitive proxies for photocarrier generation efficiency, mobility, and trap-state dynamics. Numerous studies have reported varied photoconductivity (PC) responses in 2D materials, such as normal PC, persistent PC (PPC), and negative PC (NPC), which are commonly attributed to intrinsic defects and surface-adsorbed molecules.^{34–37} PPC refers to a long-lived conductive state that persists even after illumination is removed, whereas NPC denotes a reduction in conductivity upon light exposure. Among these, PPC, defined as the prolonged conductivity after light-off, typically arises from deep-level trap states and may enhance multi-electron photocatalytic reactions by extending the lifetime of photogenerated electrons.^{36,38} Despite its mechanistic significance, PPC remains largely underexplored in the context of dynamic defect–adsorbate–carrier coupling under photocatalytic conditions.

Our prior work extended *in situ* PC to gas-phase catalysis using carbon-doped SnS₂ under CO₂/H₂O, but PPC-specific behaviors were not systematically examined.³⁹ Notably, PPC has been reported in doped and nanostructured indium oxide systems, where defect-mediated trapping correlated with enhanced catalytic yields in gas-phase reverse water–gas shift (RWGS) reactions under CO₂ + H₂.^{40,41} Their integration of *operando* PC characterization confirmed a positive correlation between PPC and catalytic performance. Although the RWGS system involves photothermal catalysis rather than pure photoexcited processes, its persistent photoconductivity behavior under illumination highlights the relevance of defect-assisted charge dynamics and supports the use of *operando* PC as a valuable mechanistic tool. To date, however, atomically thin 2D semiconductors have not yet been systematically evaluated for PPC behavior under realistic PCCO₂RR conditions nor has the modulation of PPC *via* defect–adsorbate coupling been clarified. Furthermore, despite the growing number of review articles on *in situ* characterization techniques for photocatalysis,^{29,30,42,43} *in situ* PC remains underutilized as a mechanistic probe, particularly in the case of PPC. Its capacity to resolve dynamic defect kinetics, long-lived charge retention, and interfacial electronic coupling under *operando* gas-phase conditions remains largely untapped. Addressing this knowledge gap is crucial for establishing a deeper mechanistic understanding of gas-phase photocatalysis and for developing scalable, material-agnostic PC diagnostics to screen PPC-active 2D catalysts and elucidate how defects influence CO₂ activation.



To address the critical knowledge gap in defect-adsorbate-carrier coupling under gas-phase PCCO₂RR conditions, we developed a high-sensitivity *in situ* PC platform capable of real-time monitoring of charge dynamics in defective ultrathin 2D photocatalysts. Using a 3 nm-thick MoS₂ thin film (TF) as a model system, we observed pronounced PPC under vacuum/UV exposure, attributed to approximately 5% V_S acting as deep-level traps, consistent with a 1.76 eV optical bandgap and a 0.47 eV electron capture barrier (E_c) derived from Arrhenius and configuration coordinate analyses. Upon exposure to humid CO₂/AM1.5G illumination, the photocurrent decreased by 82%, while rise and decay time constants (τ_{rise} and τ_{fall}) were significantly shortened, indicating accelerated recombination and suppressed PPC *via* enhanced adsorbate-induced electron extraction. To rationalize these observations, we propose a conceptual defect-adsorbate energy alignment model that classifies three representative coupling scenarios based on the relative position of the CO₂ LUMO and defect trap states: (i) energetic alignment, (ii) higher LUMO, and (iii) lower LUMO. Although hypothetical, this model is substantiated by experimental observations and, to the best of our knowledge, represents the first mechanistic framework linking PPC modulation to defect-adsorbate electronic interactions in ultrathin 2D photocatalysts. Beyond offering mechanistic insights, our study positions *operando* PC as a generalizable diagnostic method for probing interfacial dynamics and guiding rational defect and surface energy design for solar-driven CO₂ photocatalysis.

2. Experimental methods

2.1 Preparation and characterization of 3 nm-thick MoS₂ thin films

Three-nanometer-thick MoS₂TFs were synthesized *via* post-sulfurization of vacuum-deposited 3 nm-thick molybdenum trioxide (MoO₃) TFs using a three-zone chemical vapor deposition (CVD) system, as illustrated in Fig. S1. High-purity sulfur (99.9%, Sigma-Aldrich) and MoO₃ powder (99.95%, Alfa Aesar) were used as precursor materials. The resulting MoS₂TFs grown on SiO₂/Si substrates were characterized using a suite of microscopy and spectroscopy techniques. Atomic force microscopy (AFM, Bruker Dimension Icon) was employed to determine the film thickness and surface roughness. Optical absorbance measurements were performed using a UV-vis-NIR spectrophotometer (JASCO V-670), and the optical band gap was estimated using Tauc plots derived from the absorbance spectra. Raman and photoluminescence (PL) spectra were acquired using a Jobin-Yvon LabRAM H800 system equipped with a 532 nm Nd:YAG laser as the excitation source. The chemical composition and stoichiometry of the MoS₂TF were analyzed *via* X-ray photoelectron spectroscopy (XPS, PHI 5000 VersaProbe III) using a monochromatic Al K α source. The atomic sensitivity factors (ASFs) used for quantification were 3.544 for Mo 3d and 0.717 for S 2p, measured at a take-off

angle of 54.7°. XPS data were processed and fitted using the CasaXPS software.

2.2 Dark/photocurrent and persistent photoconductivity

The photodetector structure based on the 3 nm-thick MoS₂ TF was designed in accordance with our previous studies,^{35,39} adopting a two-terminal photoconductor configuration without gate bias. Platinum (Pt) top electrodes were deposited onto the MoS₂TF by sputtering. The ohmic behavior of the metal-semiconductor contact was verified using linear current-voltage (I - V) characteristics. All electrical measurements were carried out using a low-leakage current probe station (Lake Shore Cryotronics TTP4) integrated with a semiconductor characterization system (Keithley 4200-SCS). Dark and photocurrent responses were measured in vacuum at room temperature under illumination using three monochromatic light sources: a 375 nm ultraviolet (UV) laser, a 633 nm He-Ne laser, and an 808 nm diode laser. A constant DC bias of 1.0 V was applied during these measurements. To investigate PPC, the 3 nm-thick MoS₂TF sample was mounted on the cold finger of a closed-cycle helium cryostat, and PPC measurements were performed under 375 nm UV laser illumination at varying temperatures.

2.3 *In situ* photoconductivity measurements

In situ photoconductivity measurements were designed to probe the environmental sensitivity of the 3 nm-thick MoS₂TF device. Specifically, the photocurrent was measured in real-time while systematically varying the ambient conditions—from high vacuum ($\sim 1 \times 10^{-4}$ torr) to a mixed gas environment consisting of CO₂ and H₂O at 1 atm. These measurements were conducted under continuous AM1.5G simulated solar illumination and an applied bias of 1.0 V, as illustrated in Fig. S2. Additional experimental details related to the dark/photocurrent, *in situ* photocurrent, and PPC characterization are available in our previous reports.^{35,36,39}

2.4 Photocatalytic CO₂ reduction measurement

A 3 nm-thick MoS₂TF was evaluated for its photocatalytic CO₂ reduction performance under a 24-hour illumination period. The gaseous products generated from the PC-CO₂RR process were analyzed using a gas chromatography system (Agilent 6890) equipped with a flame ionization detector (FID) and a glass PLOT column (RT-Q-BOND). This analytical configuration enabled reliable separation and quantification of the reaction products. Further information regarding the GC system setup and reaction conditions can be found in our earlier publications.⁴⁴

3. Results and discussion

3.1 Conceptual design of the *in situ* photocurrent platform for gas-phase CO₂ photocatalysis

To systematically investigate charge transport and photocarrier retention in ultrathin 2D photocatalysts under solar-driven



gas-phase PCCO₂RR conditions, we developed a high-sensitivity *in situ* photoconductivity platform capable of real-time electrical probing under simulated solar illumination and controlled atmospheres (Fig. 1). As shown in Fig. 1a, ultrathin MoS₂TF was selected as a model photocatalyst due to its atomically thin structure, strong light–matter interaction, and the presence of intrinsic defects characteristic of 2D MoS₂, making it a promising system for real-time mechanistic studies.

To achieve this, we established an experimental configuration that combines steady-state AM1.5G illumination with a gas-phase reactor enabling exposure to reactive CO₂ + H₂O mixtures. The planar photodetector architecture (Fig. 1b) allows for direct and continuous photocurrent monitoring without the need for a gate electrode, enabling real-time tracking of charge transport while the catalyst interacts with surface adsorbates. A constant bias voltage of 1.0 V was applied during all measurements to maintain stable current collection. This configuration provides not only real-time conductivity measurements but also establishes a mechanistic foundation for correlating dynamic electrical responses with interfacial gas–solid processes. In particular, it enables time-resolved tracking of PPC modulation and interfacial electron extraction, both of which are critical for elucidating the coupling between photo-generated carriers, intrinsic defect states, and surface-adsorbed species. Such *operando*-compatible diagnosis is essential for deciphering the mechanistic basis of defect-adsorbate–carrier interactions in ultrathin 2D photocatalysts for solar-driven CO₂ reduction. The material characteristics and defect properties of the ultrathin MoS₂TF used in this study are described in the following section.

3.2 Fabrication and multimodal characterization of 3 nm MoS₂ photocatalytic films

The 3 nm-thick MoS₂TFs were synthesized by post-sulfurization of 3 nm-thick MoO₃ TF, following our previously established method.^{44,45} Initially, MoO₃ TFs were deposited onto SiO₂/Si substrates by thermal evaporation. These were then annealed at 500 °C for 1 hour under an Ar–H₂ (4 : 1) atmosphere at ~1 Torr to convert MoO₃ into MoO₂. Post-sulfuriza-

tion was conducted under Ar–H₂ (10 : 1) at 1 Torr, with sulfur powder heated to 140 °C and the substrate heated to 900 °C. After 10 minutes of reaction, MoO₃ was fully converted into MoS₂ (Fig. S1). The resulting 3 nm-thick MoS₂TF grown on SiO₂/Si substrates is shown in Fig. 2a. Optical microscopy and AFM confirmed the formation of a continuous, large-area film (Fig. 2b and c). The film thickness was measured to be approximately 3.0 nm, and the root-mean-square surface roughness (R_q) was 0.48 nm, determined *via* AFM height profiling on a scratched region (Fig. 2c). These results demonstrate the successful fabrication of uniform ultrathin films with smooth surfaces suitable for electronic measurements.

Raman spectroscopy verified the 2H-MoS₂ phase, revealing two characteristic peaks corresponding to the in-plane (E_{2g}^1 , 382.8 cm⁻¹) and out-of-plane (A_{1g} , 407.5 cm⁻¹) vibrational modes of Mo–S bonding (Fig. 2d). The Si substrate peak appeared at ~521 cm⁻¹. To further assess spatial uniformity, Raman spectra were collected from 16 positions across a 2 × 1 cm² area. The frequency difference between the A_{1g} and E_{2g}^1 modes remained consistent at ~24.7 cm⁻¹, indicating excellent thickness homogeneity (Fig. 2e). For comparison, spectra from commercial monolayer and bulk MoS₂ crystals were also included. Optical absorption properties were analyzed using UV–vis–NIR spectroscopy (Fig. 2f). Three distinct excitonic features were observed at 669, 618, and 444 nm, corresponding to the A, B, and C excitons, respectively. The inset of Fig. 2f shows a Tauc plot estimating the optical band gap at ~1.76 eV. Temperature-dependent photoluminescence (PL) spectra were recorded over the 550–800 nm range (Fig. 2g), displaying A and B exciton emissions. PL intensity increased with decreasing temperature from room temperature to 80 K, indicating reduced non-radiative recombination.

XPS was used to analyze the chemical composition and stoichiometry of the MoS₂TF. High-resolution spectra of the Mo 3d and S 2p regions are shown in Fig. 2h and i, respectively. The Mo 3d spectrum displayed two main peaks at 229.4 eV ($3d_{5/2}$) and 232.5 eV ($3d_{3/2}$), along with a small S 2s peak at 226.6 eV (Fig. 2h).^{46,47} The S 2p spectrum exhibited a doublet at 162.2 eV ($2p_{3/2}$) and 163.4 eV ($2p_{1/2}$), characteristic of Mo–S

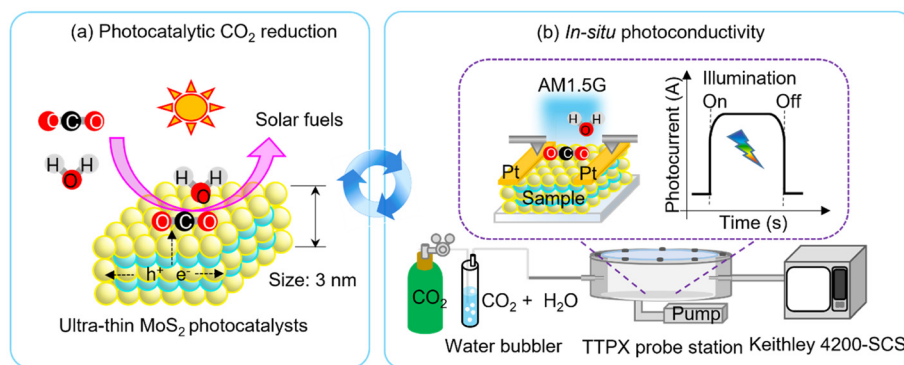


Fig. 1 (a) Schematic illustration of a 3 nm-thick MoS₂TF serving as a model photocatalyst for the solar-driven PCCO₂RR. (b) A planar MoS₂TF-based photodetector architecture for *in situ* photocurrent measurement, enabling real-time electrical probing of carrier dynamics and defect–adsorbate interactions under the solar-driven gas-phase PCCO₂RR.



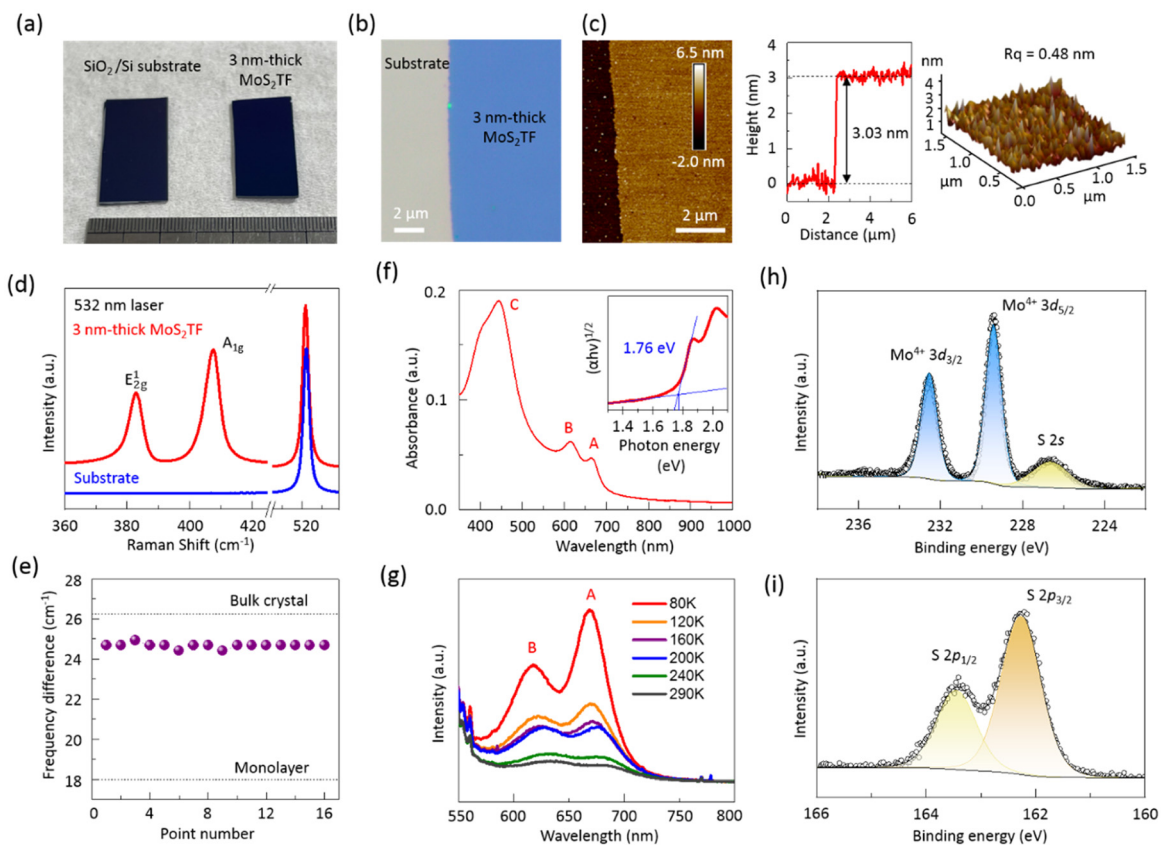


Fig. 2 (a) Photographs of the SiO₂/Si substrates before (left) and after (right) the growth of the 3 nm-thick MoS₂TF. (b) Optical microscopy image and (c) atomic force microscopy (AFM) images of the as-grown 3 nm-thick MoS₂TF, including surface height profiles and surface roughness characterization on the SiO₂/Si substrate. (d) Raman spectra of the 3 nm-thick MoS₂TF and the bare SiO₂/Si substrate, recorded using a 532 nm excitation laser. (e) Statistical distribution of the frequency difference between the A_{1g} and E_{2g}¹ Raman modes obtained from 16 different points on the 3 nm-thick MoS₂TF. Distributions from commercial monolayer and bulk MoS₂ crystals are included for comparison. (f) UV-vis-NIR absorption spectrum and (g) temperature-dependent photoluminescence (PL) spectra of the 3 nm-thick MoS₂TF. The inset in (f) shows the Tauc plot used to estimate the optical band gap. (h and i) High-resolution XPS spectra of the Mo 3d (h) and S 2p (i) core-level regions for the 3 nm-thick MoS₂TF on the SiO₂/Si substrate.

bonding (Fig. 2i).^{46–48} Quantitative XPS analysis yielded an S:Mo atomic ratio of 1.9, suggesting the presence of ~5% V_S in the film. The complete XPS survey spectrum is presented in Fig. S3. Overall, this comprehensive characterization confirmed the successful synthesis of ultrathin MoS₂TF with controlled thickness, uniform morphology, and well-defined chemical composition. These attributes are essential prerequisites for subsequent investigations of their intrinsic photoconductive properties and photocatalytic behavior.

3.3 Intrinsic photoconductivity of 3 nm-thick MoS₂TF

3.3.1 Wavelength- and power-dependent photoconductivity behavior. The intrinsic photoconductive properties of the 3 nm-thick MoS₂TF were systematically investigated under vacuum at room temperature. The experimental setup is shown in Fig. S2a. All current-voltage and time-resolved measurements were conducted with a constant bias voltage of 1.0 V. Linear and symmetric *I*-*V* curves confirmed good ohmic contact with the platinum electrodes in both vacuum and CO₂ + H₂O gas environments (Fig. S2b). Fig. 3 shows the wave-

length-dependent photocurrent responses under three laser excitations operating at the same power (375, 633, and 808 nm, 20 mW). The light was modulated in 10-minute on/off cycles over three repetitions, and signals were baseline-corrected by subtracting the dark current (Fig. 3a-c). The photocurrent magnitude strongly depended on excitation wavelength: UV illumination (375 nm) yielded the highest response (~8 nA), followed by 633 nm (~1.9 nA) and 808 nm (~0.7 nA) (Fig. 3d). This trend is consistent with the absorption spectrum shown in Fig. 2f, in which stronger absorption results in higher photocurrent generation. Additionally, power-dependent measurements under 633 nm illumination (20–40 mW) confirmed that photocurrent increased proportionally with laser power (Fig. S4). Notably, only 375 nm excitation induced a PPC effect, characterized by a slow decay of the photocurrent after the light was turned off, as discussed in detail in section 3.3.2.

3.3.2 Persistent photoconductivity behavior in ultrathin MoS₂TF. Temperature-dependent photocurrent measurements were conducted to further examine PPC (Fig. 4). In this study,



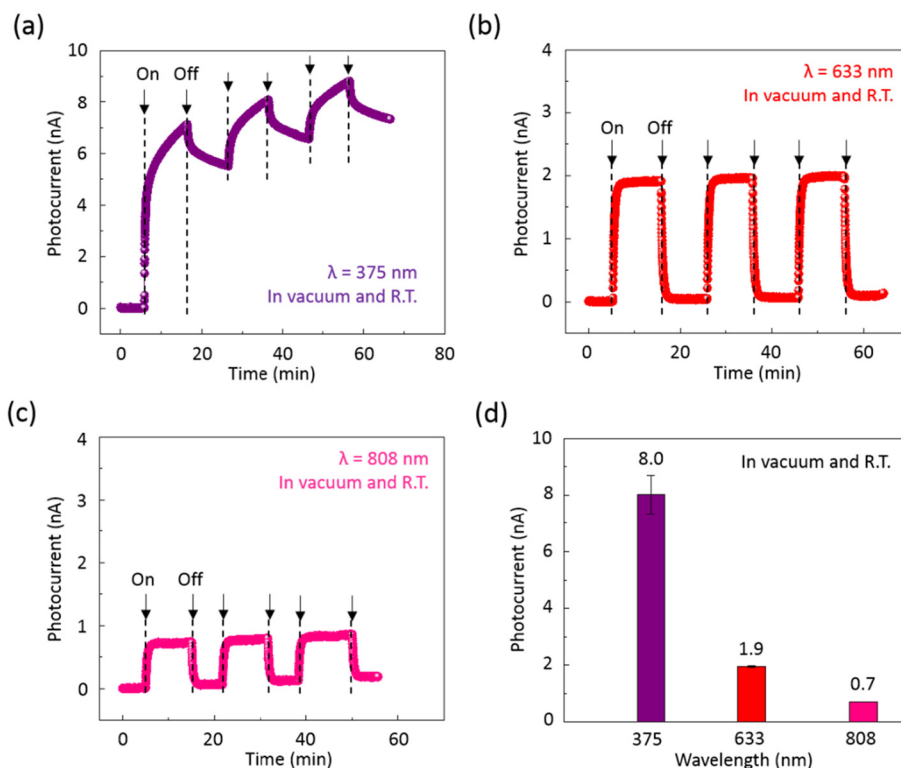


Fig. 3 Wavelength-dependent photocurrent response of the 3 nm-thick MoS₂TF under vacuum and room temperature conditions. Time-resolved photocurrent measurements were performed under laser illumination at 20 mW for three different wavelengths: (a) 375 nm (UV), (b) 633 nm (visible), and (c) 808 nm (near-infrared). (d) Averaged steady-state photocurrent values of the 3 nm-thick MoS₂TF under each wavelength, with dark current subtracted.

the PPC analysis followed established protocols for investigating defect-related conductivity and metastable carrier trapping in wide-bandgap semiconductors.^{36,49} As shown in Fig. 4a, at 150 K under 375 nm illumination and vacuum conditions, the photocurrent increased by nearly one order of magnitude and remained elevated for over 26 minutes after light-off. To assess thermal stability, a three-step temperature cycle was performed (Fig. 4b): cooling from 330 K to 150 K (current decreased), illumination at 150 K (current rose rapidly), and reheating to 330 K (current gradually returned toward the baseline). These measurements illustrate the persistence of photoexcited carriers and the metastable trapping states involved. Normalized decay curves measured at various temperatures are shown in Fig. 4c. Each curve was fitted using a stretched exponential function:⁵⁰

$$I(t) = I_{(0)} \exp[-(t/\tau)^\beta], \quad 0 < \beta < 1, \quad (1)$$

where τ is the decay time constant and β is the stretch exponent. The extracted β values (0.33–0.16) indicate a broad distribution of relaxation pathways, consistent with large lattice relaxation models.⁵¹ To quantify the thermal activation energy for carrier recapture, the temperature dependence of τ was evaluated using an Arrhenius relation:

$$\tau \propto \exp(E_c/kT), \quad (2)$$

where E_c denotes the electron capture barrier. As shown in Fig. 4d, two regimes were observed: τ decreased rapidly at higher temperatures, indicating thermally activated capture, while τ remained nearly constant at low temperatures, consistent with tunneling-assisted recombination. From the high-temperature slope, E_c was determined to be approximately 0.47 eV. This energy barrier represents the threshold required for electrons to return from the conduction band to defect states, providing a mechanistic explanation for the prolonged carrier lifetimes observed in PPC.

Finally, the configuration coordinate diagram in Fig. 4e illustrates the transition between stable deep-level states and metastable shallow donor states, offering a physical framework for interpreting the long-lived photocurrent decay. Collectively, these findings highlight that PPC in ultrathin MoS₂TF arises from defect-related metastable states, which can significantly influence charge separation and recombination processes relevant to photocatalysis.

3.4 Real-time probing of catalytic activity and PPC dynamics in ultrathin MoS₂TF

3.4.1 Photocatalytic CO₂ reduction performance. Gas-phase CO₂ photoreduction experiments were performed under simulated solar irradiation for 24 hours, with a blank control for comparison (section 2.4). As shown in Fig. 5a, the 3 nm-



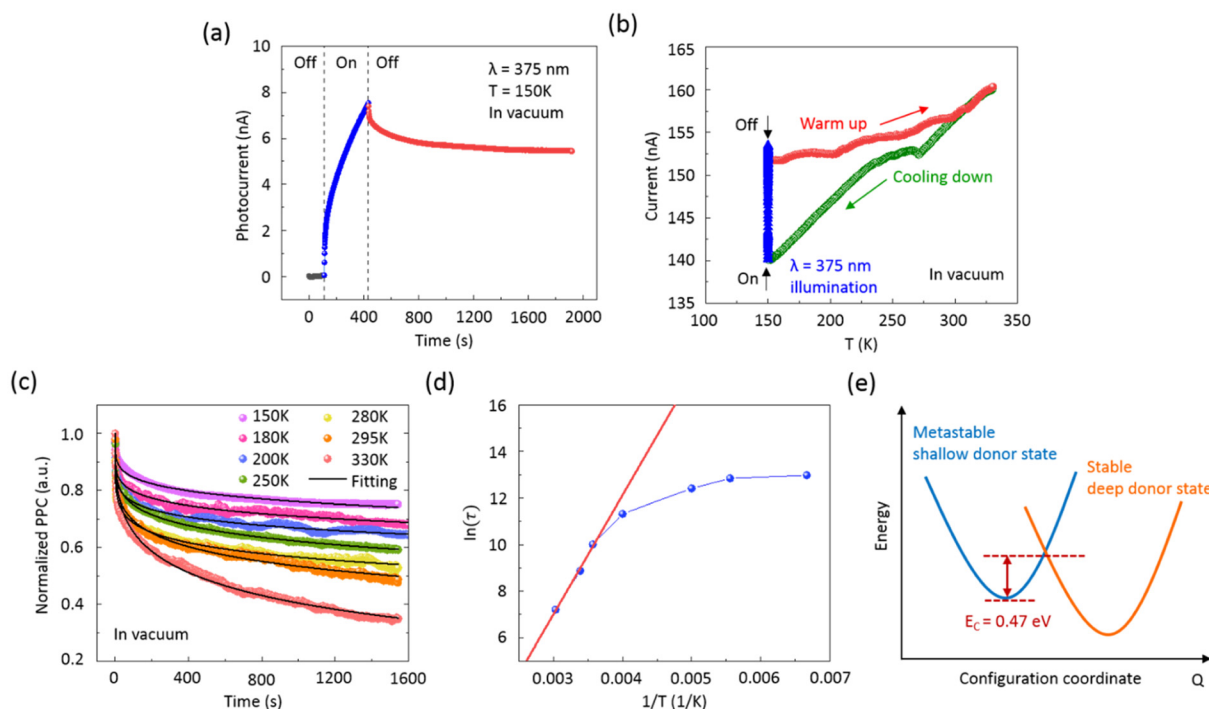
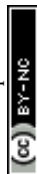


Fig. 4 Temperature-dependent PPC behavior and configuration coordinate analysis of 3 nm-thick MoS₂TF. (a) Representative PPC buildup and decay response of 3 nm-thick MoS₂TF measured at 150 K under vacuum. (b) Temperature-dependent current response of 3 nm-thick MoS₂TF before, during, and after illumination with a 375 nm laser. (c) Normalized PPC decay curves of 3 nm-thick MoS₂TF collected at different temperatures. Dark current was subtracted from all measurements. (d) Arrhenius plot of the PPC decay time constant ($\ln \tau$ versus $1/T$) for 3 nm-thick MoS₂TF. Blue spheres represent experimental data and the red line corresponds to the fit based on eqn (2). (e) Schematic configuration coordinate diagram illustrating the transition between a metastable shallow donor state (blue parabola curve) and a stable deep donor state (orange parabola curve) in 3 nm-thick MoS₂TF. E_c represents the electron capture barrier energy.

thick MoS₂TF produced methane (CH₄) and acetaldehyde (CH₃CHO), with a total yield of 431 nmol m⁻². Isotopic ¹³CO₂ reduction experiments further confirmed that CH₄ exhibited a complete ¹³C signal, and the CH₃ fragment of CH₃CHO showed ¹³C labeling, verifying their assignment as genuine CO₂ photoreduction products (Fig. S5). Although CH₃CHO exhibited only partial ¹³C incorporation (¹³CH₃ + ¹²CHO), the detection of a labeled CH₃ fragment clearly indicates that it is at least partially derived from CO₂ reduction. While film-based photocatalyst yields are typically lower than those of powder materials,^{52,53} ultrathin planar architectures offer advantages for mechanistic studies by providing well-defined interfaces and controllable defect environments. This work presents the first demonstration of gas-phase CO₂ photoreduction using an ultrathin 3 nm MoS₂TF, enabling direct correlation between catalytic output and charge dynamics. To uncover the underlying photoelectronic behavior, *in situ* photoconductivity measurements were carried out under the same reaction conditions, offering time-resolved insight into carrier dynamics and PPC modulation. Although the photocatalytic CO₂RR experiments yielded a mixture of products, reflecting the long-standing selectivity challenge of MoS₂-based systems, the primary focus of this work is to establish mechanistic insights using *operando* photoconductivity rather than to optimize

product selectivity. According to previous reports, surface modification strategies (*e.g.*, sulfur vacancy engineering and supported Au single atoms or nanoparticles) have proved effective in enhancing product selectivity in MoS₂ catalysts.^{18,19} These approaches represent promising directions for future studies aiming to improve the CO₂RR performance. With these considerations in mind, we next examine the *in situ* photocurrent response under identical CO₂RR conditions to correlate catalytic outputs with the underlying charge dynamics.

3.4.2 *In situ* photocurrent response under CO₂ reduction conditions. *In situ* photocurrent measurements were conducted to further examine the behavior of the 3 nm-thick MoS₂TF under conditions relevant to solar-driven CO₂ reduction (Fig. 5b). Experiments alternated between vacuum and humid CO₂ (CO₂ + H₂O) environments under AM1.5G illumination and a constant applied bias of 1 V. Under vacuum, the device exhibited a clear PPC behaviour (blue curve in the lower panel of Fig. 5b), characterized by a rapid initial rise in photocurrent followed by a slower increase, eventually reaching ~39.7 nA after 10 minutes of illumination. After the light was switched off, the photocurrent decayed gradually and remained at ~15.8 nA after 30 minutes in darkness. In contrast, under humid CO₂ (red curve in the lower panel of Fig. 5b), the photocurrent reached ~7 nA during illumination



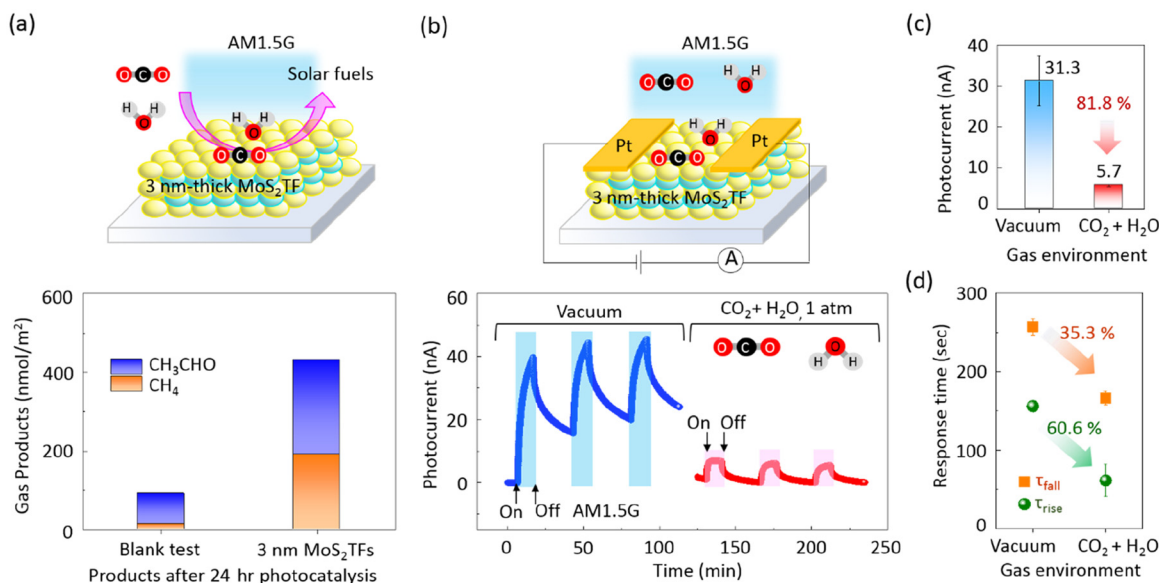


Fig. 5 Photocatalytic performance and *in situ* photocurrent response of the 3 nm-thick MoS₂TF. (a) Schematic illustration (top) of solar-driven photocatalytic CO₂ reduction using the 3 nm-thick MoS₂TF and the corresponding gaseous products (bottom) generated after 24 hours of reaction. The total gaseous products include CH₄, CH₃CHO, C₂H₄, and C₃H₆O. (b) Schematic diagram (top) of the *in situ* photoconductivity measurement platform, and the corresponding time-resolved photocurrent responses (bottom) of the 3 nm-thick MoS₂TF under two gas environments: vacuum (blue) and CO₂ + H₂O (red). (c) Comparison of the average photocurrent and (d) photoresponse time constants (τ_{rise} and τ_{fall}) under vacuum and CO₂ + H₂O conditions. All measurements were performed under AM1.5G simulated sunlight. Photocurrent values were corrected by subtracting the baseline dark current.

and decayed rapidly to ~ 1 nA after the light was turned off, indicating strong suppression of PPC due to gas-phase interactions.

Fig. 5c quantifies these differences more systematically. The average photocurrent over three illumination cycles decreased from 31.3 nA in vacuum to 5.7 nA in humid CO₂, corresponding to an $\sim 82\%$ reduction in signal amplitude. Fig. 5d presents the extracted rise and decay time constants (τ_{rise} and τ_{fall}) under both environments. In vacuum, τ_{rise} and τ_{fall} were measured as 156 s and 275 s, respectively. Under humid CO₂, they decreased to 61 s and 167 s. These values were obtained by fitting the time-resolved photocurrent transients to exponential decay functions (details in Fig. S6). Notably, τ_{rise} decreased by $\sim 60\%$, while τ_{fall} decreased by $\sim 35\%$, highlighting that humid CO₂ not only reduced photocurrent amplitude but also accelerated the temporal evolution of recombination dynamics. From a photocatalytic perspective, this decrease in photocurrent should not be regarded solely as a loss of conductivity. Rather, it reflects enhanced electron extraction by surface-adsorbed CO₂/H₂O species, indicating that photogenerated carriers are being actively utilized in CO₂ activation processes. Although the measurable signal is reduced, the observed behavior provides direct evidence that electrons are diverted away from the conductive pathway and utilized in CO₂ photoreduction reactions. To disentangle the spectral contribution to PPC, control measurements using a 633 nm laser were performed. These experiments confirmed that PPC was induced by the UV component of the AM1.5G spectrum. No

PPC behavior was observed under 633 nm illumination in either gas environment (Fig. S7).

To better understand the mechanistic implications of these observations, it is instructive to consider the physical processes associated with τ_{rise} and τ_{fall} . During illumination, electron-hole pairs are generated in the MoS₂TF. These carriers must be separated and transported to contribute to the photocurrent. The rise time constant (τ_{rise}) reflects the time required for carriers to transition from generation to formation of a steady conduction pathway. A shorter τ_{rise} indicates faster carrier extraction. Under humid CO₂, τ_{rise} decreased by $\sim 60\%$, suggesting that adsorbed CO₂ molecules may facilitate faster carrier transfer *via* additional surface channels or transient trapping sites. When illumination is turned off, carriers recombine or are captured by defect states. The decay constant (τ_{fall}) reflects carrier recombination or trapping dynamics, with shorter values indicating faster loss pathways. Under humid CO₂, τ_{fall} was $\sim 35\%$ shorter, indicating accelerated decay of the photocurrent, likely due to enhanced electron capture by adsorbed CO₂ species acting as recombination centers. Overall, these findings demonstrate that humid CO₂ exerts a dual influence: it accelerates initial carrier extraction and transport (shorter τ_{rise}) but also promotes faster recombination (shorter τ_{fall}). From a photocatalytic perspective, this dual effect may facilitate electron transfer to adsorbed reactants but could also shorten carrier lifetimes, potentially limiting overall efficiency. Such dual modulation of charge dynamics implies that surface adsorbates may influence defect-state occupancy



or depth, thereby shifting the energy landscape of photocarrier retention. These results clearly demonstrate the dynamic modulation of photocarrier behavior by surface adsorbates, reflecting a complex interplay between charge transport and recombination processes at defect-rich ultrathin interfaces. The observed shortening of τ_{rise} and τ_{fall} , along with the suppressed PPC, suggests that adsorbate-induced perturbations may influence the energetics of defect states. These observations motivate the energy-level coupling model presented in section 3.6, where defect–adsorbate–carrier interactions are explicitly rationalized to account for the observed PPC modulation and recombination kinetics.

Importantly, to the best of our knowledge, this study represents the first experimental observation of PPC in an ultrathin MoS₂TF under simulated solar-driven CO₂ reduction conditions. While prior PPC reports in MoS₂ were largely limited to field-effect transistor configurations under vacuum or inert environments,^{54–59} our results extend this understanding to *operando* gas-phase photocatalytic systems, highlighting the pivotal role of surface adsorbates in modulating defect-state energetics and photocarrier retention. This observation not only demonstrates the functional relevance of PPC in catalytically active conditions but also provides a mechanistic basis for the energy-level alignment model presented in section 3.5, where the coupling between intrinsic defects, surface adsorbates, and photocarriers is explicitly rationalized.

3.5 Photoconductivity-based mechanistic elucidation and energy-level model of defect–adsorbate–carrier coupling

In this study, we systematically employed an *in situ* photoconductivity platform to probe the microscopic interactions among intrinsic defects, surface adsorbates, and photogenerated carriers in ultrathin MoS₂ photocatalysts under simulated gas-phase PCCO₂RR conditions. This platform resolves real-time processes such as CO₂ activation, carrier generation, transport, trapping, and recombination, enabling a mechanistic foundation for rational defect engineering in 2D materials. To construct this framework, we highlight three mechanistic pillars: (i) the correlation between specific defect structures and photoconductivity behaviors; (ii) the dual modulation of charge dynamics by CO₂ adsorption; (iii) an energy-level alignment model describing how defect–adsorbate coupling governs PPC.

(i) Photoconductivity behavior serves as a sensitive indicator of defect–carrier coupling. As illustrated in Fig. 6a, four representative defect types,^{22,60} namely 0D vacancies or dopants, 1D dislocations, 2D grain boundaries, and 3D heterogeneities, can serve as catalytic sites that facilitate CO₂ adsorption and activation. However, the corresponding photoconductive responses, including normal PC, PPC, and NPC, have not yet been systematically classified (Fig. 6b). In our study, a 3 nm MoS₂ thin film containing ~5% V_S exhibited pronounced PPC under PCCO₂RR conditions. Previous spectroscopic and DFT studies have shown that V_S in MoS₂ introduce localized states below the conduction band edge.⁶¹ These divergences across

prior studies suggest that photoconductivity behavior is highly sensitive to both defect configuration and environmental gas composition. We suggest that *in situ* photoconductivity can serve as a high-throughput diagnostic tool for screening the defect–gas interactions under catalytic conditions.

(ii) Adsorbed CO₂ molecules simultaneously influence carrier extraction and recombination. Based on our measurements under humid CO₂ conditions, the photoconductivity rise and decay time constants (τ_{rise} and τ_{fall}) were shortened by approximately 60% and 35%, respectively, accompanied by a substantial decrease in steady-state PPC (Fig. 5b–d). These findings indicate that CO₂ dynamically modulates trap occupancy by interacting with defect states at the catalyst surface. Fig. 6b schematically illustrates three representative photoconductivity behaviors (Type I: PC, Type II: PPC, and Type III: NPC), each exhibiting distinct rise and decay time constants. Although only the PPC case was directly observed in our experiment, we infer that the physical parameters governing photoconductivity dynamics, such as carrier retention and recombination rates, are likely influenced by gas-phase conditions across all three types. This implies a broader research opportunity to systematically study how PCCO₂RR environments modulate photoconductivity in different defect configurations. Fig. 6c further bridges the photoelectronic response to molecular events, depicting CO₂ photoactivation *via* electron injection into its LUMO ($2\pi_u$), forming bent CO₂^{•−} intermediates.^{8,21} Although this classic mechanism does not explicitly include defects, we expand it by proposing that adsorbate–defect coupling alters interfacial charge transfer and carrier lifetimes through energy-level interaction.

(iii) To interpret the role of defects in modulating PPC, we propose a conceptual energy-level alignment model (Fig. 6d), which relates the LUMO energy level of adsorbed CO₂ to the energetic position of defect-induced trap states. The model considers three representative alignment scenarios. In Scenario I, the CO₂ LUMO is energetically aligned with the trap states introduced by V_S, enabling efficient electron transfer from the defect to the adsorbate and thereby depleting trapped carriers, which leads to suppression of PPC. In Scenario II, the CO₂ LUMO lies above the defect level, resulting in unfavorable electron injection and prolonged carrier trapping, thus sustaining the PPC effect. In Scenario III, the LUMO of CO₂ resides below the defect energy level, allowing rapid extraction of electrons from the traps and consequently causing an abrupt quenching of PPC. This alignment-based interpretation provides a new perspective on how sulfur-vacancy-derived trap states modulate photoconductivity *via* interaction with adsorbed molecules. Although the model remains conceptual, further validation through density functional theory (DFT) simulations or band-alignment measurements such as XPS and ultraviolet photoelectron spectroscopy (UPS) is warranted to quantitatively assess the proposed scenarios, towards a coherent framework linking defect energetics with gas-phase carrier dynamics. Such DFT and XPS/UPS studies are beyond the scope of this study.



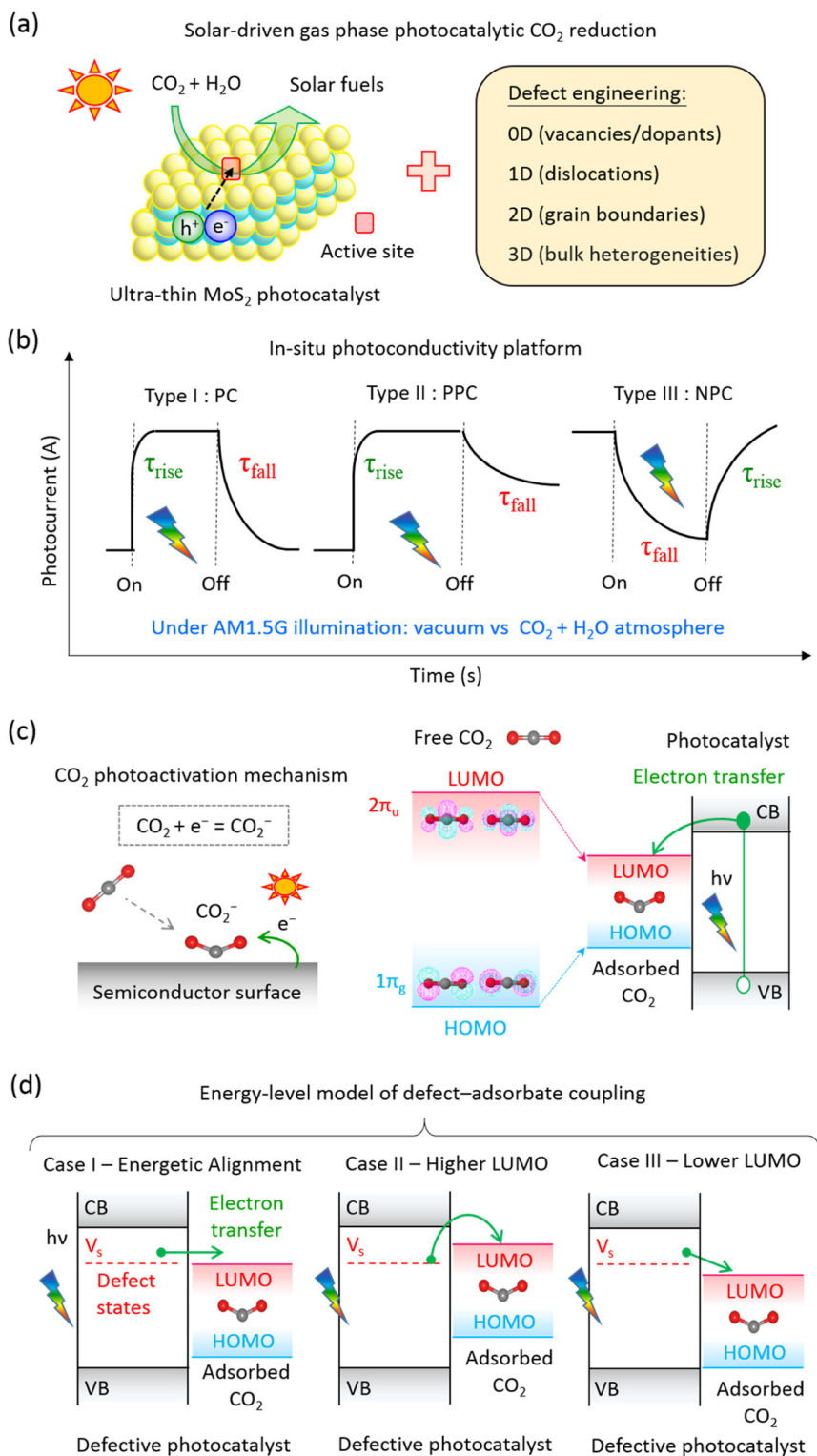


Fig. 6 Mechanistic framework of defect-adsorbate-carrier coupling in ultrathin MoS₂TF for solar-driven CO₂ reduction. (a) Schematic of gas-phase CO₂ photoreduction using defect-engineered ultrathin MoS₂TF, highlighting four catalytic defect classes: 0D (vacancies/dopants), 1D (dislocations), 2D (grain boundaries), and 3D (bulk heterogeneities). (b) An *in situ* photoconductivity platform for classifying MoS₂ photoconductivity under PCCO₂RR conditions (AM1.5G + CO₂/H₂O), enabling identification of Type I (PC), Type II (PPC), and Type III (NPC) behaviors, along with analysis of photocurrent and response times (τ_{rise} and τ_{fall}). (c) CO₂ photoactivation mechanism, where photogenerated electrons are injected into the CO₂ LUMO ($2\pi_u$), generating bent CO₂⁻ intermediates and triggering redox reactions. (d) Proposed energy-level alignment model based on sulfur vacancies (V_s), illustrating how defect-adsorbate coupling modulates PPC: Scenario I – aligned energy levels promote electron transfer, quenching PPC; Scenario II – higher LUMO prevents transfer, sustaining PPC; Scenario III – lower LUMO rapidly extracts electrons, leading to rapid PPC decay. This model provides a mechanistic foundation for understanding defect-adsorbate-carrier interactions and guiding photocatalyst design.



To our knowledge, this is the first mechanistic model that directly links defect–adsorbate–carrier coupling to measurable PPC behavior in ultrathin 2D photocatalysts under solar-driven CO₂ reduction. Such insights may guide future defect engineering strategies aimed at optimizing carrier lifetimes and interfacial reactivity. This platform could also be extended to explore how tailored defect densities, surface chemistries, and band alignments affect photocatalyst performance.

4. Conclusions

In this study, we developed a high-sensitivity *operando* PC platform to investigate persistent photoconductivity (PPC) in ultrathin MoS₂TF under simulated solar-driven CO₂ photoreduction conditions. Our results revealed that sulfur vacancies (~5%) act as deep-level traps that drive PPC under vacuum/UV light conditions, evidenced by a 1.76 eV bandgap and 0.47 eV electron capture barrier. Under humid CO₂, an 82% drop in photocurrent and shortened rise/decay constants indicated enhanced charge extraction by adsorbates, leading to PPC suppression. To rationalize these observations, we proposed a hypothetical energy-level alignment model that conceptually links defect states with the electronic structure of adsorbed CO₂. This represents the first *operando* mechanistic demonstration of PPC regulation in 2D photocatalysts during gas-phase CO₂ activation. Beyond providing mechanistic insight, our *operando* PC strategy offers a scalable diagnostic and rational design basis for defect-engineered screening and optimization of next-generation solar-driven CO₂ reduction catalysts. Future integration of *in situ* PC with theoretical modeling or XPS/UPS measurements may further validate this framework and unlock defect-specific design rules for predictive catalyst development.

Author contributions

Shang-Wei Ke: investigation, data curation, and formal analysis. Chih-Yang Huang: investigation, data curation, and formal analysis. Yi-Fan Huang: conceptualization, investigation, data curation, formal analysis, writing – original draft, writing – review & editing, and supervision. Yun-Hsuan Chan: data curation. Rwei-San Chen: resources, funding acquisition, and supervision. Kuei-Hsien Chen: resources, funding acquisition and supervision. Li-Chyong Chen: resources, funding acquisition, writing – original draft, writing – review & editing, and supervision.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article are included in the supplementary information (SI). Supplementary information is available. See DOI: <https://doi.org/10.1039/d5nr03394b>.

Additional information is available from the corresponding authors upon reasonable request.

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