

Light-enhanced hydrogen spillover on Pt/TiO₂ catalysts for efficient flow reverse water-gas shift reaction

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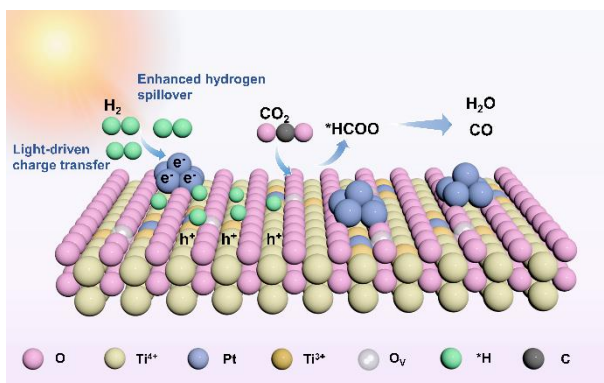
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We demonstrate light-enhanced hydrogen spillover on Pt/TiO₂ for efficient RWGS reaction. Photogenerated electron transfer from TiO₂ to Pt creates electron-rich Pt sites that promotes H₂ dissociation, while hole-rich TiO₂ facilitates active hydrogen migration. This synergy triggers enhanced hydrogen spillover, generating more oxygen vacancies and active hydrogen on TiO₂ surface, thereby shifting reaction path to *HCOO. Consequently, Pt/TiO₂ catalyst achieves a high CO production rate of 30.51 mol·g_{Pt}⁻¹·h⁻¹ under a mild light-driven condition (Xe lamp, 2.5 W/cm², 283 °C). Even in harsh outdoor environments (−20.7 °C) using only concentrated sunlight, comparable performance can be achieved. This work offers a new paradigm for achieving efficient solar-driven catalysis.

Light-enhanced hydrogen spillover on Pt/TiO₂ catalysts for efficient flow reverse water-gas shift reaction

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ABSTRACT: Hydrogen spillover is a key process governing the efficiency and selectivity of CO₂ hydrogenation reactions. Although various static catalyst structural design strategies have been developed for promoting this process, this dynamic regulation by external stimuli has rarely been achieved. Herein, we demonstrate the light-enhanced hydrogen spillover on Pt/TiO₂ and its critical role in catalyst regulation and performance enhancement for RWGS. Under light irradiation, photogenerated electrons transfer from TiO₂ to Pt, making Pt electron-rich to promote H₂ dissociation, while hole on TiO₂ surface promote active hydrogen migration. This synergistic charge redistribution induces a light-enhanced hydrogen spillover, creating abundant oxygen vacancies and delivering more active hydrogen. Consequently, light-driven RWGS process proceeds via a *HCOO-mediated pathway, different from the thermal-driven process. Using light as the sole energy source (2.5 W/cm²), Pt/TiO₂ catalyst achieves a CO production rate of 30.51 mol·g_{Pt}⁻¹·h⁻¹ with 99.12% CO selectivity in a continuous-flow system at a mild catalyst surface temperature (283 °C), outperforming most thermal and photothermal catalysts. Remarkably, comparable performance is achieved using only concentrated sunlight even under outdoor temperature of −20.7 °C. This work establishes a new paradigm for dynamic charge transfer controlling spillover effects in solar-driven catalysis.

KEYWORDS: light-enhanced hydrogen spillover, charge redistribution, Pt/TiO₂, reaction pathway modulation, reverse water-gas shift

1 Introduction

Reverse water-gas shift (RWGS) reaction enables CO₂ conversion to CO, a critical feedstock for producing high-value chemicals and liquid fuels via Fischer-Tropsch processes, thus offering a feasible pathway for carbon resource utilization and carbon neutrality [1]. Traditionally, RWGS reaction demands the high reaction temperatures (often exceeding 500 °C) to overcome the kinetic barriers of CO₂ activation [2]. This high-temperature operation often results in substantial energy consumption and catalyst deactivation, which remain long-standing challenges for practical applications. Supported catalysts, particularly Pt/TiO₂ system, have been established as highly efficient thermal catalysts for RWGS, benefiting from the synergistic interaction between Pt sites and oxygen vacancies (O_v) on TiO₂ [3, 4]. Specifically, Pt sites facilitate hydrogen dissociation, whereas adjacent O_v is responsible for CO₂ adsorption and activation [5, 6]. Notably, the migration efficiency of the active hydrogen species from Pt sites to O_v or other active sites on the TiO₂ support directly governs the reaction rate of CO₂ hydrogenation, which is a process known as hydrogen spillover [7-9].

Hydrogen spillover refers to the migration of active hydrogen species from metal surfaces to oxide supports, which can significantly improve catalyst activity, selectivity, and stability [10, 11]. Enhancing this effect requires synergistic optimization

of two aspects: H₂ dissociation on the metal and subsequent hydrogen migration on the support. The efficiency of H₂ dissociation strongly depends on the dispersion state and electronic structure of the metal, for which the electron-rich metal centers often promote back-donation into H₂ antibonding orbitals to enhance H₂ dissociation [12, 13]. Meanwhile, the migration ability of hydrogen species on the support can be facilitated by strategies such as tuning support electronic properties or creating oxygen vacancies [14, 15]. To this end, researchers have developed various strategies to promote hydrogen spillover [16]. On one hand, metal site regulation, such as introducing secondary metals to form alloys (e.g., Pt-Pd, Ni-Cu), enhances hydrogen dissociation and migration through synergistic metal interactions [17]. On the other hand, support engineering, such as using supports with high surface areas and suitable pore structures, introducing oxygen vacancies in reducible oxides (e.g., TiO₂, CeO₂), or heteroatom doping materials, significantly promotes hydrogen migration by lowering diffusion barriers [18]. In addition, metal-support interface engineering, such as constructing specific metal-oxide interfaces, core-shell structures, or bimetallic interfaces, can effectively lower the energy barrier for hydrogen atom migration from metal to support [19]. However, these approaches are inherently static. Once synthesized, the catalyst's hydrogen spillover behavior is dictated by its equilibrium structure under thermal conditions, fundamentally limiting the enhancement

achievable through such static design. This limitation calls for a dynamic, non-equilibrium approach to modulate hydrogen spillover beyond what is possible under thermal equilibrium.

Light irradiation offers a particularly intriguing avenue to address these limitations. Light can provide a dynamic modulation that can transiently alter both the electronic structure of metal sites and the defect chemistry of the support. When the semiconductor-based materials, such as TiO_2 , are illuminated, the spatial separation and localized accumulation of photogenerated charge carriers are generated [20], which can be harnessed to tailor catalytic interfaces in ways that are difficult to achieve under thermal equilibrium conditions. Recent studies have demonstrated that light irradiation can induce charge carrier transfer to enable site separation in semiconductor-supported metal catalysts, such as in Pd/SrTiO_3 where electron-rich Pd promotes H_2 dissociation and suppresses alkyne adsorption, while holes on SrTiO_3 enhance substrate adsorption and hydrogen migration [21]. Such photoinduced charge redistribution achieves efficient, selective spillover hydrogenation of alkynes to olefins, which is difficult to achieve for conventional static strategies. Therefore, if photogenerated charge carriers can be directed to modulate the metal and support structure, this may provide a non-equilibrium pathway to enhance hydrogen spillover for the efficient RWGS reaction. However, whether such light-promoted hydrogen spillover can be realized for RWGS, and particularly how it might be harnessed during the catalyst formation stage to create superior active sites, remains largely unexplored.

Herein, we report a light-driven Pt/TiO_2 catalyst that exhibits greatly enhanced hydrogen spillover for the structural optimization of catalyst and improved RWGS performance. Light irradiation drives electron transfer from TiO_2 to Pt. This leaves Pt sites enriched with electrons, which accelerates H_2 cleavage, and simultaneously generates a TiO_2 surface enriched with holes that actively facilitates the migration of active hydrogen species. The resulting, light-enhanced hydrogen spillover not only generates a high density of O_v on TiO_2 to promote the adsorption/activation of CO_2 molecules, but also supplies abundant active hydrogen to the support surface, accelerating the hydrogenation of reaction intermediates and steering the RWGS reaction toward the $^*\text{HCOO}$ -mediated pathway. Using light as the sole energy source, a localized catalyst surface temperature of about 283°C is achieved ($2.50\text{ W}/\text{cm}^2$) and the CO_2 conversion can reach 28.01% in a continuous-flow system, significantly higher than that under thermal-driven conditions (6.71%, 283°C). A high CO production rate of $30.51\text{ mol}\cdot\text{g}_{\text{Pt}}^{-1}\cdot\text{h}^{-1}$ with the CO selectivity of 99.12% can be achieved, superior to some reported catalysts operating under high-temperature conditions. Importantly, this system can also achieve the good performance even under harsh outdoor conditions (-20.7°C) using only concentrated sunlight. This work demonstrates the feasibility of light-enhanced hydrogen spillover for efficient CO_2 conversion and provides a new paradigm for the development of solar-driven energy conversion platforms.

2. Experimental

2.1. Chemical Materials

Tetrabutyl titanate (TBOT, $\geq 99\%$) and platinum(II) chloride hexahydrate ($\text{H}_2\text{PtCl}_6\cdot 6\text{H}_2\text{O}$) were purchased from Shanghai

Aladdin Biochemical Technology Co., Ltd. N,N -dimethylformamide (DMF, analytical grade), isopropyl alcohol (IPA, analytical grade), and ethanol (analytical grade) were purchased from Tianjin Fuyu Fine Chemical Co., Ltd., and ethylenediamine (EDA, 99.5%) was purchased from Shandong Xiya Chemical Co., Ltd. All chemicals and materials were purchased commercially and were unpurified.

2.2. Material Preparation:

Preparation of the $\text{H}_2\text{Ti}_2\text{O}_5\cdot\text{nH}_2\text{O}$: The multi-edged $\text{H}_2\text{Ti}_2\text{O}_5\cdot\text{nH}_2\text{O}$ sphere precursor was synthesized by a facile solvothermal reaction. In a typical synthesis, 30 mL of IPA was vigorously stirred with 10 mL of DMF at 500 rpm for 30 min. After that, 1.0 mL of TBOT was added to the mixed solvent and stirred for 2 h. Then, the mixed solution was transferred to a 100 mL Teflon-lined stainless-steel autoclave and heated in an electric oven at 200°C for 20 h. The resultant product was separated by centrifugation, washed with distilled water for five times and ethanol for two times, and dried at 60°C for 12 h.

Preparation of the $\text{Pt}/\text{TiO}_2\text{-Pre}$: 1.2 g $\text{H}_2\text{Ti}_2\text{O}_5\cdot\text{nH}_2\text{O}$ precursor was refluxed with 6 mL of EDA and 120 mL of H_2O aqueous solution at 85°C for 38 h. Then, 8 mL of $\text{H}_2\text{PtCl}_6\cdot 6\text{H}_2\text{O}$ solution ($1.5\text{ mg}\cdot\text{mL}^{-1}$) was dispersed in 10 mL H_2O , which was further added into the above homogeneous solution and stirred for 10 h. The resultant product was separated by centrifugation, washed with distilled water for three times and ethanol for one time, and dried at room temperature for 24 h. The product was further calcined under air atmosphere at 450°C for 2 h with a heating ramp of $1.5^\circ\text{C}\cdot\text{min}^{-1}$.

Preparation of the Pt/TiO_2 : This sample was prepared by *in-situ* reconstruction of the $\text{Pt}/\text{TiO}_2\text{-Pre}$ during a light-driven or thermal-driven RWGS reaction. For the light-driven sample, the light intensities were ranging from $2.05\text{--}3.00\text{ W}/\text{cm}^2$ with an irradiation time of 60 minutes. Typically, the *in-situ* reconstructed sample under $2.50\text{ W}/\text{cm}^2$ is named as $\text{Pt}/\text{TiO}_2\text{-LD}$. For thermal-driven samples, the temperatures were ranging from $237\text{--}322^\circ\text{C}$ with a heat treatment time of 60 minutes; the *in-situ* reconstructed sample under 283°C is named as $\text{Pt}/\text{TiO}_2\text{-TD}$. In addition, $\text{Pt}/\text{TiO}_2\text{-Pre}$ was treated with H_2 at 300°C for 2 hours to obtain $\text{Pt}/\text{TiO}_2\text{-300H}$ catalyst.

2.3. Catalytic performance evaluation:

CO_2 hydrogenation activity was evaluated in a continuous-flow reactor with a circular quartz window (Shinsco Instrument Co., Ltd.) at atmospheric pressure. Initially, 40 mg catalyst was uniformly coated onto a glass fiber sheet with a diameter of 18 mm. The catalyst-loaded glass fiber was then placed into the stainless-steel reactor, and a reaction gas containing CO_2+H_2 (1:3) was introduced ($48\text{ mL}/\text{min}$). After 30 min, a full spectrum 300 W Xe lamp equipped with a collecting lens served as the light source to illuminate the catalyst through a quartz window on the top of the catalyst. The light intensity on catalyst surface was measured using an optical power meter and the temperature of catalyst surface was monitored by a thermocouple and a thermal imager. The temperature of the reaction chamber was monitored by a thermocouple inserted therein.

The effluent gas (the transfer lines were heated and maintained at 120°C to avoid condensation of the product H_2O) was automatically and periodically injected into a gas chromatograph (Techcomp Scion 456i) equipped with a flame ionization detector (FID) using Ar as carrier gas and a thermal

conductivity detector (TCD) using H_2 as carrier gas. When the reaction was stable, the concentrations of CO_2 and products (including CO , CH_4 and some C_2 - C_5 hydrocarbons) in the effluent gas were analyzed. Identity and quantitation of products were determined by external standard method calibrated by the standard gas mixture.

The CO_2 conversion, the selectivity and production rate of CO at different gas hourly space velocities (GHSV, 2.4 - 48 ($\times 10^4$) $mL \cdot g^{-1} \cdot h^{-1}$) and light intensity (2.05 - 3.00 W/cm^2) were calculated according to the following equations:

$$\text{External std } CO_2 \text{ conversion (\%)} = \frac{[CO_2]_{in} - [CO_2]_{out}}{[CO_2]_{in}} \times 100\% \quad (1)$$

$$CO \text{ selectivity (\%)} = \frac{[CO]_{out}}{[CO]_{out} + [CH_4]_{out} + [C_xH_y]_{out}} \times 100\% \quad (2)$$

$$\text{Rate } CO \text{ (mol} \cdot g_{Pt}^{-1} \cdot h^{-1}) = \frac{[CO]_{out}}{N_A \times m_{cat} \times L_{Pt} \times h} \quad (3)$$

Furthermore, the carbon balance of the reaction was calculated under various light intensities based on the following formula.

$$C_{bal} (\%) = \frac{[CO_2]_{out} + [CO]_{out} + [CH_4]_{out}}{[CO_2]_{in}} \quad (4)$$

Where $[CO_2]_{in}$ and $[CO_2]_{out}$ represent the contents of CO_2 in the inlet gas and outlet gas, respectively. $[CO]_{out}$, $[CH_4]_{out}$, and $[C_xH_y]_{out}$ represent the contents of CO , CH_4 and hydrocarbons in the outlet gas (in the actual measurement, only CO and CH_4 were detected, while the content of the hydrocarbons was negligible). N_A is the Avogadro constant, m_{cat} is the catalyst loading mass and h is the reaction time.

To verify the accuracy of the performance measurements, N_2 was introduced into the feed gas as an internal standard ($CO_2/H_2/N_2=24/72/4$) and CO_2 conversion was calculated using the internal standard method on another gas chromatograph (Techcomp Scion 456C) equipped with two flame ionization detectors (FID) and a thermal conductivity detector (TCD) using

Ar as carrier gas.

$$\text{Inner std } CO_2 \text{ conversion (\%)} = \frac{[CO_2]_{in} - [CO_2]_{out}}{[CO_2]_{in}} = \left[1 - \frac{A_{out}(CO_2) \times A_{in}(N_2)}{A_{in}(CO_2) \times A_{out}(N_2)} \right] \times 100\% \quad (5)$$

Where $A_{in}(CO_2)$ and $A_{in}(N_2)$ refer to the chromatographic peak area of CO_2 and N_2 in the feed gas, and $A_{out}(CO_2)$ and $A_{out}(N_2)$ refer to the chromatographic peak area of CO_2 and N_2 in the outlet gas, respectively.

2.4. Materials characterization:

All the characterization methods were in this work were listed in Supporting Information.

3. Result and Discussion

3.1. Synthesis and Characterization of Pt/TiO₂

The Pt/TiO₂ catalyst is constructed via *in-situ* reconstruction of the pre-catalyst during the light or thermal-driven RWGS reaction, as illustrated in Figure 1a. The resulting catalysts are denoted as Pt/TiO₂-LD and Pt/TiO₂-TD, respectively. Initially, a flower-like TiO₂ precursor (TiO₂-P, $H_2Ti_2O_5 \cdot nH_2O$) with a large specific surface of 110.16 m^2/g is synthesized via a facile solvothermal method (Figure S1-S2, Table S1) [22]. Subsequently, an amine-assisted anchoring strategy is employed to achieve effective assembly of Pt species on TiO₂-P surface (Pt/TiO₂-P). After calcination under air atmosphere, TiO₂-supported PtO_x pre-catalyst (Pt/TiO₂-Pre) is obtained. This pre-catalyst is directly used for light/thermal-driven RWGS reaction.

The catalytic performance of the Pt/TiO₂ catalysts was evaluated in a continuous-flow reactor under atmospheric pressure. The CO_2 conversion was calculated using the external standard method and further verified by the internal standard method, confirming the accuracy of the performance data (Figure S3 and Table S2). The carbon balance under different conversion levels exceeds 98.28%, demonstrating excellent closure of the carbon mass balance (Table S3).

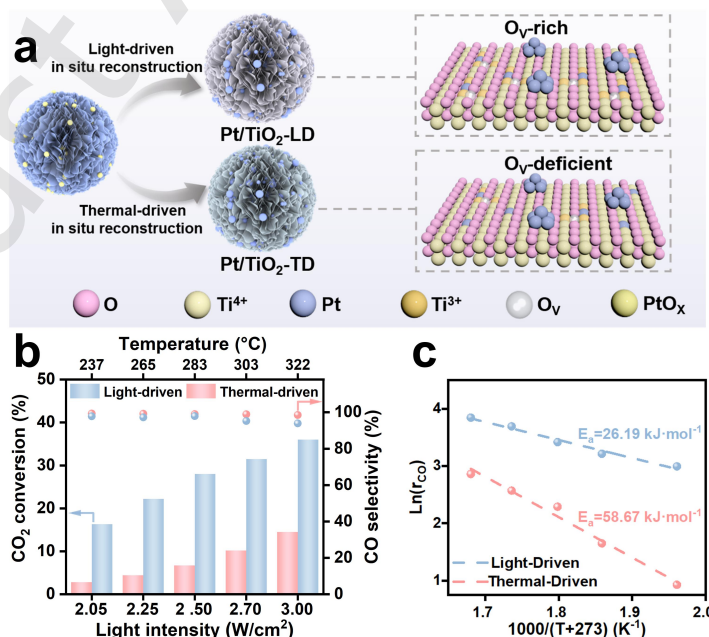


Figure 1. (a) Schematic illustration of the Pt/TiO₂ catalyst via *in-situ* reconstruction, (b) CO_2 conversion and CO selectivity of the Pt/TiO₂ catalyst at different light intensities and temperatures (thermal catalysis), (c) Arrhenius plots of CO production rates for the Pt/TiO₂ catalyst under light-driven and thermal catalytic conditions.

For the light-driven RWGS reaction, the performance evaluation is conducted under irradiation intensities ranging from 2.05 to 3.00 W/cm², which the catalyst surface temperature reaches 237 to 322 °C (Figure 1b). The CO₂ conversion rises from 16.32% to 36.04% as the irradiation intensity increases. To isolate the contribution of light from that of heating, the thermal catalytic performance is evaluated at the same surface temperatures under dark conditions. Under thermal-driven conditions, the CO₂ conversion increases from 2.83% to 14.50% as the reaction temperature rises from 237 to 322 °C. The CO₂ conversion under light-driven conditions is significantly superior to that under thermal-driven conditions at equivalent surface temperatures. Typically, at an irradiation intensity of 2.50 W/cm², the catalyst surface temperature reaches 283 °C, yielding a CO₂ conversion of 28.01%, approximately 4.17 times higher than that under thermal-driven conditions (283 °C, 6.71%). The CO selectivity reaches 97.89% under light-driven conditions and 99.03% under thermal-driven conditions. It is worth noting that under light irradiation, the light-driven heating effect is confined to the catalyst surface, where temperatures reach 237–322 °C, whereas the reactor cavity remains at only 40–50 °C. This stands in stark contrast to the traditional thermal catalysis, which requires bulk heating of the entire reactor to achieve comparable reaction temperatures. Such localized heating not only improves energy utilization efficiency but also enhances operational safety. In addition, the apparent activation energy (E_a) of above two processes is also calculated at relatively low conversion levels (below 15%). As shown in Figure 1c, the E_a of the light-driven catalytic process is 26.19 kJ·mol⁻¹, significantly lower than that of the thermal catalysis process (58.67 kJ·mol⁻¹). The superior catalytic efficiency and lower activation energy of the light-driven process strongly imply the formation of a unique catalyst surface structure under light irradiation, distinct from that obtained through thermal activation.

The differences in microstructures of Pt/TiO₂-LD and Pt/TiO₂-TD catalysts constructed via *in-situ* reconstruction of the pre-catalyst during the light or thermal-driven RWGS reaction are further investigated. The X-ray diffraction (XRD) patterns (Figure 2d) shows that Pt/TiO₂-LD and Pt/TiO₂-TD catalysts only exhibit the characteristic peaks of anatase TiO₂. The absence of Pt characteristic peaks might be due to the low content and/or small Pt particle size (Pt contents are 1.67 wt.% and 1.73 wt.% determined by inductively coupled plasma atomic emission spectroscopy, (ICP-OES, Table S4). Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images show that above two catalyst both maintain the flower-like structure composed of the interconnected nanosheets (Figure 2a,2b and Figure S4). Meanwhile, N₂-adsorption-desorption-tests also display the similar specific surface areas for above two catalysts (100.25 m²/g for Pt/TiO₂-LD and 105.81 m²/g for Pt/TiO₂-TD, (Figure S5-S6 and Table S1). The magnified TEM images display the lattice fringes (lattice spacing of 0.35 nm) corresponding to TiO₂ (101) planes and no Pt species are observed (Figure S7). CO adsorption diffuse reflectance infrared transform spectroscopy (CO-DRIFTS) is used to identify the existential state of Pt species on TiO₂ surface. As shown in Figure 2e, Pt/TiO₂-LD and Pt/TiO₂-TD catalysts show the similar CO peak distribution, indicating the similar Pt structure for above two catalysts. The dominant peak at 2027–2032 cm⁻¹ attributed to linearly adsorbed CO and the weak peak at 1800–1825 cm⁻¹ attributed to bridge-bonded CO on metallic Pt sites are simultaneously observed, suggesting the existence of small-sized Pt clusters. In addition, there is also a linearly adsorbed CO peak (2066–2076 cm⁻¹) on oxidized Pt species (Pt^{δ+}) [23]. This means the existence of single-atom Pt species in addition to Pt clusters. Above results suggest that Pt/TiO₂-LD and Pt/TiO₂-TD catalysts both present the coexistence structure of Pt clusters and atomically dispersed Pt species.

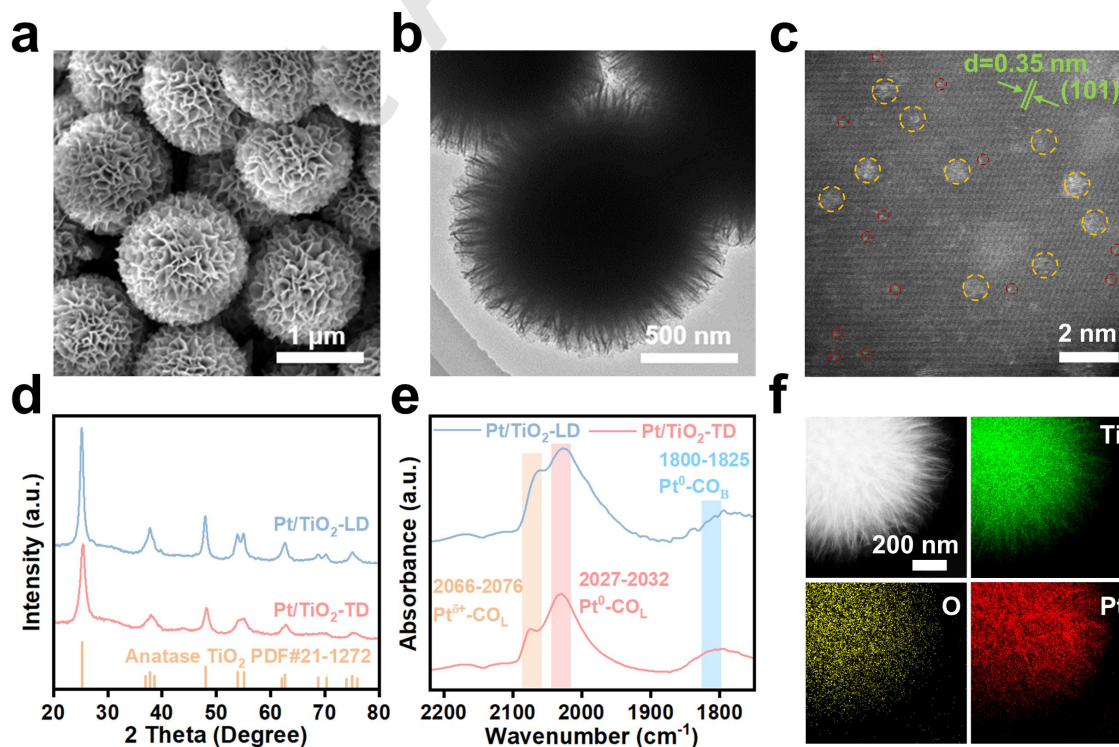


Figure 2. (a-c) SEM, TEM, and HAADF-STEM images of Pt/TiO₂-LD, (d) XRD patterns of Pt/TiO₂-LD and Pt/TiO₂-TD, (e) CO-DRIFTS spectra of Pt/TiO₂-

LD and Pt/TiO₂-TD catalysts, (f) STEM images of Pt/TiO₂-LD and the corresponding element distribution.

The high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image of Pt/TiO₂-LD catalyst provide visualized evidence. As illustrated in Figure 2c, Pt clusters about 0.50-1.50 nm are uniformly distributed on TiO₂ surface, accompanied by a small number of atomically dispersed Pt species. Elemental mapping further confirms the uniform distribution of Pt, Ti and O elements across Pt/TiO₂-LD catalyst (Figure 2f). The electronic structure and coordination environments of Pt species are further investigated via X-ray photoelectron spectroscopy (XPS) and X-ray absorption fine structure (XAFS) measurements. As shown in Figure 3a, the Pt/TiO₂-LD and Pt/TiO₂-TD catalysts exhibit the similar Pt 4f XPS spectra, indicating the similar surface chemical states and Pt structures. Taking Pt/TiO₂-LD catalyst as an example, the predominant peaks at 70.6/73.8 eV (48%) are assigned to Pt⁰ species. The remaining two pairs of peaks at 72.1/75.4 and 74.8/78.0 eV are assigned to Pt²⁺ and Pt⁴⁺ species, respectively, derived from atomically dispersed Pt species [24, 25]. These Pt 4f XPS results are consistent with the CO-DRIFTS and HAADF-STEM observations, further confirming the coexistence of Pt clusters and atomically dispersed Pt species in both Pt/TiO₂-LD and Pt/TiO₂-TD catalysts.

XAFS measurements further give more structural information about Pt species for Pt/TiO₂-LD catalyst. Figure 3b displays the normalized X-ray absorption near-edge structure (XANES) structure of Pt L₃-edge. The white-line peak and absorption edge of Pt/TiO₂-LD are between those of Pt foil and PtO₂ reference, suggesting that the Pt species exhibit an average oxidation state between 0 and +4, which is attributed to the coexistence of Pt clusters and atomically dispersed Pt species for Pt/TiO₂-LD catalyst [26, 27]. Further analysis of the Fourier-transform (FT)

extended X-ray absorption fine structure (EXAFS) spectrum (Figure 3c) reveals the local coordination environment of Pt. Among them, the Pt-Pt coordination arises from Pt clusters and the Pt-O coordination comes from the combined contribution of atomically dispersed Pt species and highly dispersed Pt clusters (Pt-TiO₂ interfaces). The pronounced Pt-O coordination peak, along with the weak Pt-Pt coordination peak, confirms the coexistence of Pt clusters and single atoms for Pt/TiO₂-LD catalyst. Furthermore, Figure 3d and Figure S8 show the EXAFS fitting curves for Pt/TiO₂-LD in the R-space and K-space; the detailed fitting parameters are listed in Table S5. The Pt-Pt coordination number is 1.50 with the bond length of 3.14 Å, markedly different from that of Pt foil (coordination number of 12 and bond length of 2.76 Å), further evidencing the Pt nanocluster features. Wavelet transform (WT) contour plots (Fig. 3e-g) confirm the Pt-O and Pt-Pt coordination structures in Pt/TiO₂-LD catalyst, supporting the coexistence of Pt single atoms and clusters.

The above results show that Pt/TiO₂-LD and Pt/TiO₂-TD catalysts possess similar Pt structure with the coexistence of Pt clusters and Pt single atoms on TiO₂ surface. Therefore, the significant performance differences of two catalysts in light/thermal-driven RWGS reaction may attributable to the different surface properties of TiO₂ supports, such as O_v. Figure 4a shows the O 1s XPS spectra of Pt/TiO₂-LD and Pt/TiO₂-TD catalysts, which can be deconvoluted into three peaks at 529.7, 530.5, and 532.0 eV, corresponding to the lattice oxygen (O_L), O_v species, and surface OH species, respectively [28]. Pt/TiO₂-LD exhibits a higher O_v/O_L ratio (0.27) than Pt/TiO₂-TD catalyst (0.21), indicating a higher concentration of O_v.

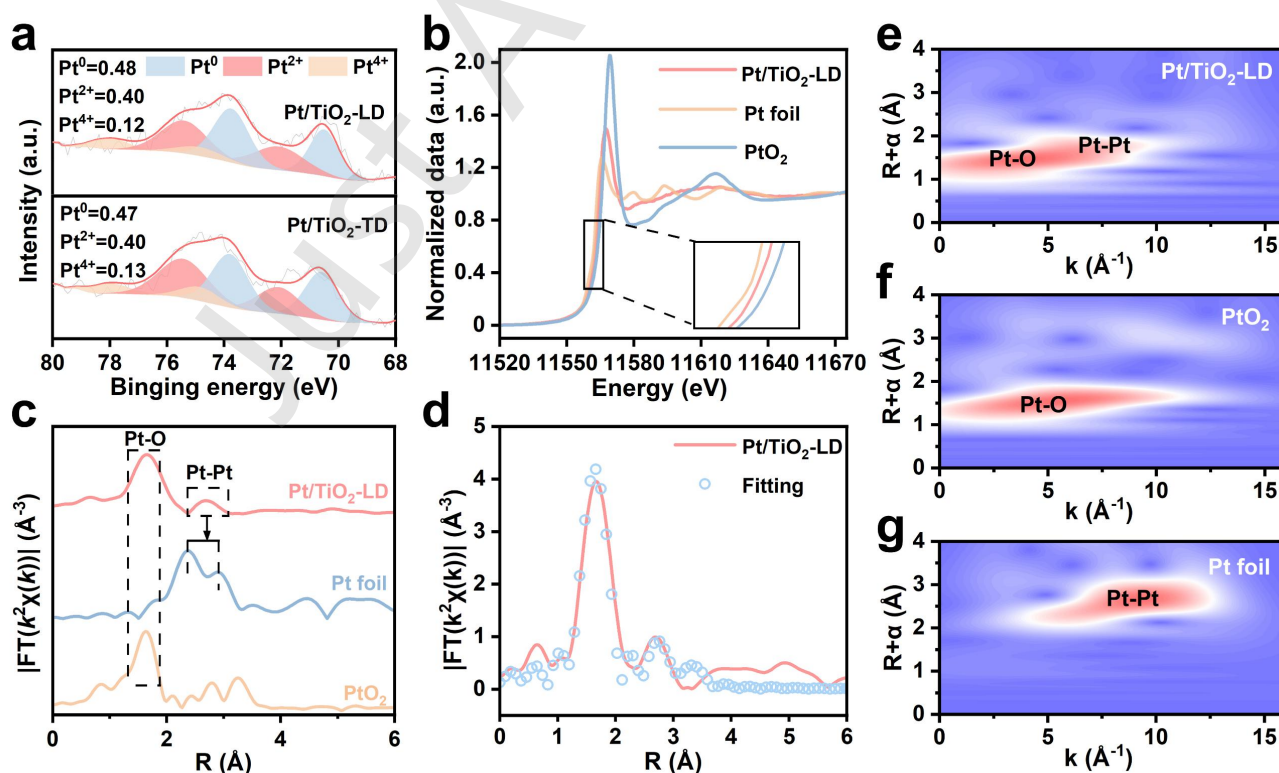


Figure 3. (a) Pt 4f XPS spectra of Pt/TiO₂-LD and Pt/TiO₂-TD catalysts, (b) XANES spectra of the Pt L₃-edge over the Pt/TiO₂-LD, Pt foil and PtO₂, (c) Fourier-transform EXAFS spectra of Pt/TiO₂-LD, Pt foil, and PtO₂, (d) Fourier-transformed amplitude of the Pt L₃ edge EXAFS spectrum for Pt/TiO₂-LD in R

space, (e-g) Wavelet transforms of the EXAFS signals for Pt/TiO₂-LD, PtO₂, and Pt foil.

Ti 2p XPS spectra further corroborate this observation. As shown in Figure 4b, in addition to the dominant Ti⁴⁺ signal peak at 464.2/458.5 eV, a shoulder peak at 462.8/457.4 eV attributable to Ti³⁺ species is identified for Pt/TiO₂-LD catalyst [29, 30]. This is consistent with the enhanced concentration of O_V in Pt/TiO₂-LD catalyst. The electron paramagnetic resonance (EPR) spectra provide more direct evidence for O_V. As shown in Figure 4c, Pt/TiO₂-LD catalyst exhibits a stronger EPR signal peak at $g = 2.001$ than Pt/TiO₂-TD catalyst, further confirming the higher concentration of O_V in Pt/TiO₂-LD [31, 32]. The enhanced amount of O_V in the Pt/TiO₂ catalyst plays a crucial role in modulating its electronic structure and light absorption properties. As shown in Figure 4d, UV-visible diffuse reflectance spectroscopy (UV-vis DRS) reveals that the Pt/TiO₂-LD catalyst exhibits significantly enhanced absorption in the visible region (400-800 nm) compared to the Pt/TiO₂-TD catalyst, indicating more efficient utilization of sunlight. The bandgap of Pt/TiO₂-LD, determined via the Tauc plot method, is calculated to be 2.11 eV, which is narrower than that of Pt/TiO₂-TD (2.34 eV). This narrowing is attributed to the higher concentration of O_V in Pt/TiO₂-LD, which introduce defect states within the bandgap of TiO₂. Consequently, the narrowed bandgap facilitates the generation of photogenerated charge carriers under visible-light irradiation, which is essential for achieving high-efficiency light-driven catalysis.

The higher concentration of O_V in the light-driven catalyst is attributed to the light-enhanced hydrogen spillover. To verify this, light-assisted H₂ temperature-programmed desorption (H₂-TPD) experiments for Pt/TiO₂-LD catalyst are conducted, in which light was introduced at the H₂ adsorption stage. As shown in Figure 5a, the H₂-TPD curves consist of two regions: the low-temperature desorption peaks (below 250 °C) are assigned to hydrogen species adsorbed on Pt sites (Pt-H), and the high-

temperature desorption peak (250-500 °C) corresponds to hydrogen species that have migrated to the TiO₂ support (spillover H) [33, 34]. Under light irradiation, the Pt/TiO₂-LD catalyst exhibits a larger hydrogen desorption peak compared to that under dark conditions, which is mainly contributed by the enhanced desorption of spillover H species. This directly demonstrates that light irradiation promotes the hydrogen spillover effect on Pt/TiO₂-LD catalyst. Furthermore, as shown in Figure S10, the light-enhanced hydrogen spillover effect is also observed on Pt/TiO₂-TD catalyst. This suggests that this promoting effect is a general response for Pt/TiO₂ systems. The light-enhanced hydrogen spillover is further evidenced by WO₃ colorimetric experiments, as WO₃ can be readily reduced by spilled hydrogen species to form blue H_xWO₃ [35]. As shown in Figure 5b, pure WO₃ shows only a slight color change after thermal (283 °C) or light-driven (2.50 W/cm²) treatment in H₂ flow, which is attributed to mild reduction by H₂ gas rather than by spilled hydrogen. In contrast, a physical mixture of the Pt/TiO₂-pre catalyst with WO₃ undergoes a significant color change after H₂ treatment. Under thermal-driven conditions (283 °C), the mixture turns light gray, indicating limited hydrogen spillover. Under light-driven conditions (2.50 W/cm²), the mixture turns deep blue, indicating that light irradiation substantially promotes hydrogen spillover and leads to the formation of more H_xWO₃. W 4f XPS analysis was performed on the catalyst-WO₃ mixture after the colorimetric experiments (Figure S11). The semi-quantitative results show that the W⁵⁺/W⁶⁺ ratio of light-driven sample (0.21) is significantly higher than that of thermal-driven sample (0.06), confirming that light irradiation significantly enhances the hydrogen spillover efficiency and promotes the reduction of WO₃ [36].

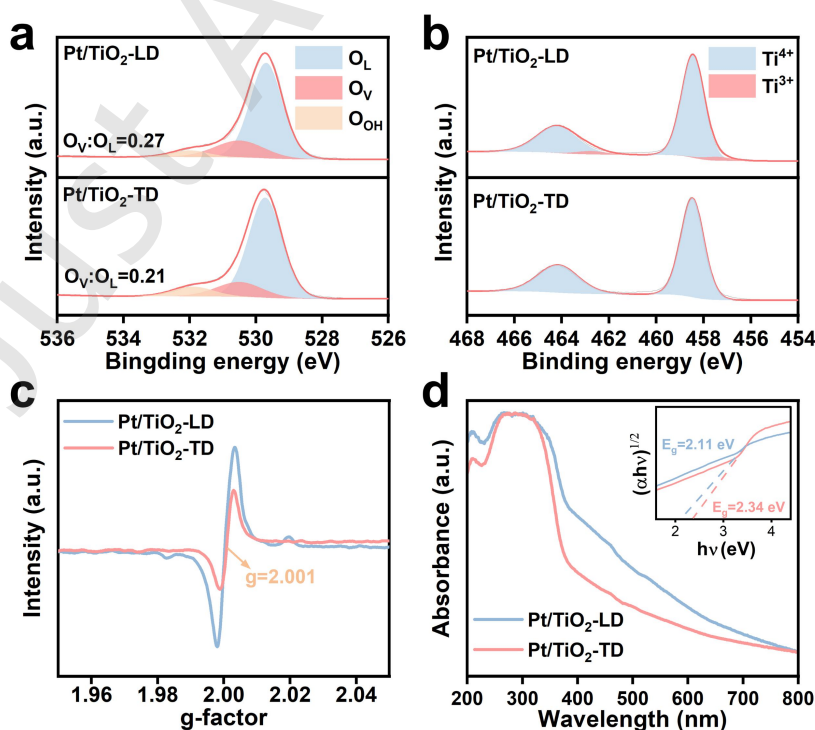


Figure 4. O 1s XPS spectra (a), Ti 2p XPS spectra (b), EPR spectra (c), and diffuse reflect UV-vis absorption spectra (d) of Pt/TiO₂-LD and Pt/TiO₂-TD catalysts.

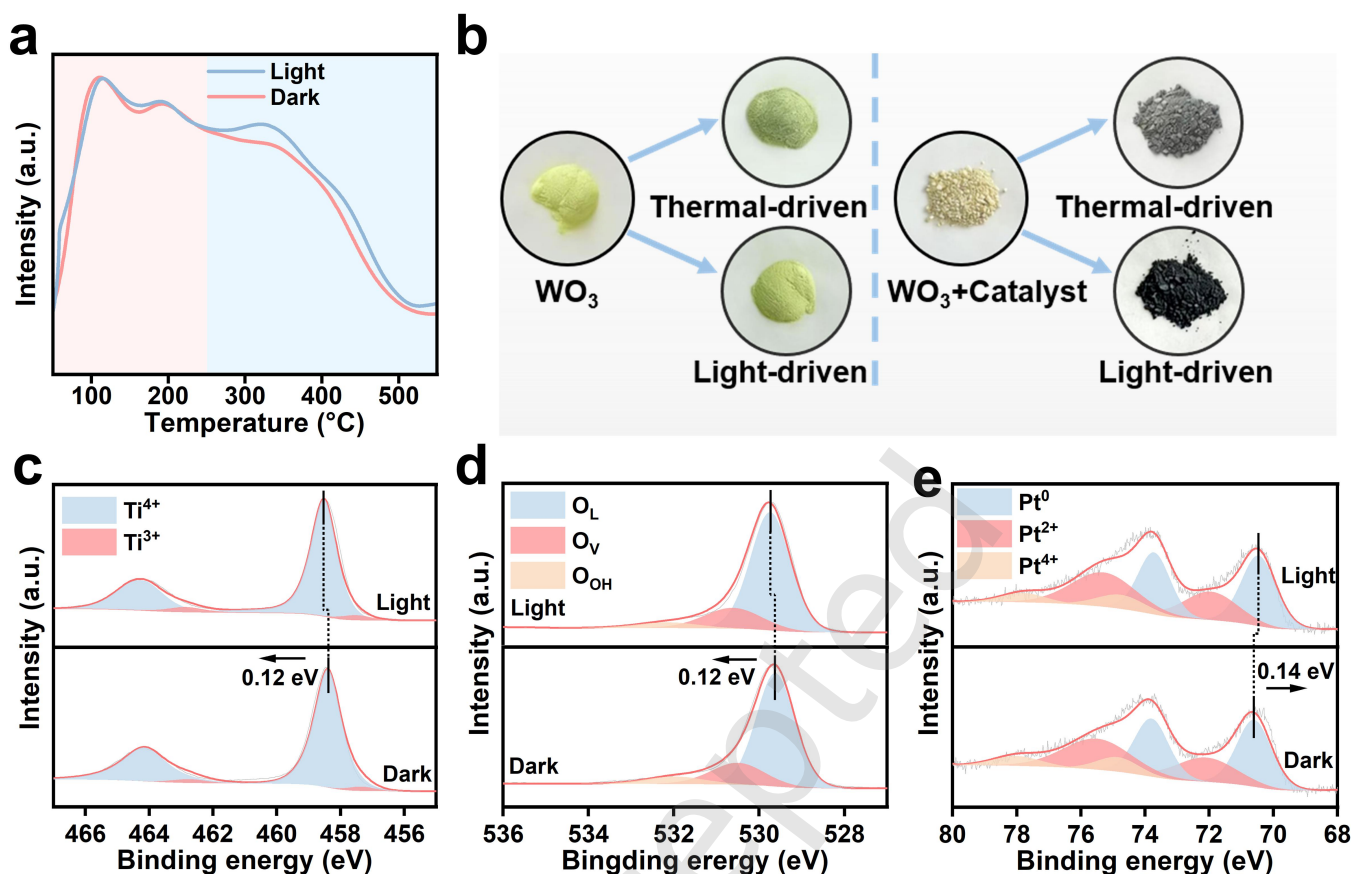


Figure 5. (a) H₂-TPD curves of Pt/TiO₂-LD under light and dark conditions, (b) Photographs of Pt/TiO₂ and WO₃ mixtures or pure WO₃ following thermal-driven or light-driven treatment in CO₂ and H₂, (c) Ti 2p, (d) O 1s, and (e) Pt 4f XPS spectrum of Pt/TiO₂ under dark and light irradiation conditions.

To elucidate the origin of the light-induced enhancement of hydrogen spillover in the Pt/TiO₂-LD catalyst, the surface charge variation under light irradiation was investigated by *in-situ* irradiation XPS (ISI-XPS). As shown in Figure 5c-e and Table S6, upon light irradiation, the binding energies of O 1s and Ti 2p shift positively by 0.12 eV, while the Pt 4f binding energy exhibits a significant negative shift of 0.14 eV. This result indicates that photogenerated electrons migrate from TiO₂ to Pt sites, leading to electron accumulation on Pt and concurrent hole accumulation on TiO₂ surface [1, 37]. CO-DRIFTS was performed on Pt/TiO₂-LD under both dark and light irradiation conditions. As shown in Figure S12, the CO adsorption peak on Pt/TiO₂-LD exhibits a red shift upon illumination, indicating an increase in electron density on the Pt surface [21, 38]. To further elucidate the charge transfer dynamics, time-resolved photoluminescence (TRPL) measurements were performed on both Pt/TiO₂-LD and bare TiO₂-LD reference samples. The Pt/TiO₂-LD sample exhibits a shorter average photoluminescence lifetime ($\tau_{\text{avg}} = 2.88$ ns) compared to bare TiO₂-LD ($\tau_{\text{avg}} = 5.98$ ns) (Figure S13 and Table S7), confirming the presence of an additional electron transfer pathway from TiO₂ to Pt [39]. This light-induced charge redistribution plays a vital role in promoting hydrogen spillover. On one hand, the electron-rich Pt sites can facilitate H₂ dissociation: the increased electron density on Pt promotes back-donation into the antibonding orbitals of H₂, lowering the dissociation barrier and generating abundant active hydrogen species [21]. On the other hand, the positively charged TiO₂ surface, resulting from hole accumulation, promotes the

migration of hydrogen species [40]. The interplay between electron-rich Pt sites and the positively charged TiO₂ support synergistically boosts the overall hydrogen spillover efficiency.

The above results confirm that light-enhanced hydrogen spillover promotes the catalyst reconstruction during the light-driven RWGS reaction, thereby forming of the Ov-rich Pt/TiO₂-LD catalyst. To investigate the contribution of light-enhanced hydrogen spillover to the performance enhancement, a control experiment using a pre-reduced Pt/TiO₂ catalyst (300 °C H₂ treatment for 2 h, denoted as Pt/TiO₂-300H) was conducted. The results shown in Figure S14 indicate that Pt/TiO₂-300H catalyst achieves a CO₂ conversion of 28.71% under light-driven conditions (2.5 W/cm², 273 °C), significantly superior to the 8.53% conversion achieved under thermal-driven conditions (273 °C). These results suggest that catalyst reconstruction-induced Ov-rich structure provides a favorable foundation for the RWGS reaction, and the light-enhanced hydrogen spillover effect further delivers an additional and substantial performance boost.

3.2 Light-enhanced Hydrogen Spillover Modulates RWGS Reaction Pathway

To further explore the influence of light-enhanced hydrogen spillover on the reaction pathway of RWGS reaction, *in-situ* diffuse reflectance Fourier transform infrared spectroscopy (*in-situ* DRIFTS) experiments are conducted under both light-driven and thermal-driven conditions. As shown in Figure 6a and Figure S15, after exposing the Pt/TiO₂ catalyst to the reaction atmosphere (CO₂:H₂=1:3) for 30 min in dark condition,

characteristic vibrational peaks corresponding to carboxylate species (*COOH , 1630 cm^{-1}), bidentate carbonate (b-CO_3^{2-} , 1305 cm^{-1}), and monodentate carbonate (m-CO_3^{2-} , 1405 cm^{-1}) are predominantly observed [35, 41, 42]. However, upon light irradiation, (2.5 W/cm^2 , catalyst surface temperature $238\text{ }^\circ\text{C}$, Figure S16) *COOH signal progressively weakens and disappears, while the new signal peaks corresponding to formate species (*HCOO , 1364 , 1394 , and 1578 cm^{-1}) and bicarbonate (HCO_3^- , 1687 cm^{-1}) emerge and intensify with increasing reaction time, suggesting that *HCOO serves as a key reaction intermediate under light-driven conditions [43, 44]. In contrast, under purely thermal-driven conditions ($237\text{ }^\circ\text{C}$), the *in-situ* DRIFTS spectrum shows only the *COOH intermediate characteristic peaks. This indicates that the light-driven RWGS reaction proceeds via *HCOO pathway, which is distinct from the *COOH pathway observed under thermal-driven conditions. Given that the *in-situ* DRIFTS measurements under both light-driven and thermal-driven conditions were performed at identical catalyst surface temperatures ($\sim 237\text{ }^\circ\text{C}$), the reaction pathway switch is intrinsically driven by the photochemical effect, rather than a thermal artifact. Moreover, as shown in Figures S17–18, neither variations in light intensity (1.80 – 2.25 W/cm^2) nor changes in reaction temperature (205 and $237\text{ }^\circ\text{C}$) affect the respective reaction pathways: *HCOO intermediates remain dominant under light-driven conditions, while *COOH intermediates are consistently observed under thermal-driven conditions. These results further corroborate the above conclusions.

Based on the comprehensive experimental evidence, we propose a complete catalytic mechanism for the light-driven

RWGS reaction on the Pt/TiO_2 catalyst, as illustrated in Figure 6c. The switch of the reaction pathway from *COOH (under thermal-driven conditions) to *HCOO (under light-driven conditions) is primarily attributed to the light-enhanced hydrogen spillover effect. As established by ISI-XPS, light-assisted H_2 -TPD, and WO_3 colorimetric experiments, photoexcitation drives electron transfer from TiO_2 to Pt, creating electron-rich Pt sites and hole-rich TiO_2 surface. The electron-rich Pt sites facilitate H_2 dissociation, while the holes accumulated on TiO_2 promote the migration of active hydrogen species. This synergistic optimization enhances the entire hydrogen spillover process, resulting in a high local concentration of active hydrogen on the TiO_2 surface. The enhanced hydrogen spillover removes more oxygen atoms from the TiO_2 surface, forming more O_v , which in turn boost CO_2 adsorption and activation.

Under these conditions, activated CO_2 is rapidly hydrogenated by spillover hydrogen to form abundant *HCOO intermediates, which are subsequently converted to CO . This light-driven mechanism stands in stark contrast to the thermal pathway, where the limited hydrogen availability forces the reaction to proceed via the *COOH pathway. Thus, the light-enhanced hydrogen spillover increases the abundance of active hydrogen, effectively couple catalyst structure optimization with rapid intermediate hydrogenation, and avoids the bottlenecks inherent to conventional thermal catalysis. This synergistic interplay between light-induced charge transfer, hydrogen spillover, catalyst reconstruction, and reaction pathway modulation provide a comprehensive explanation for the superior RWGS performance of the light-driven Pt/TiO_2 catalyst.

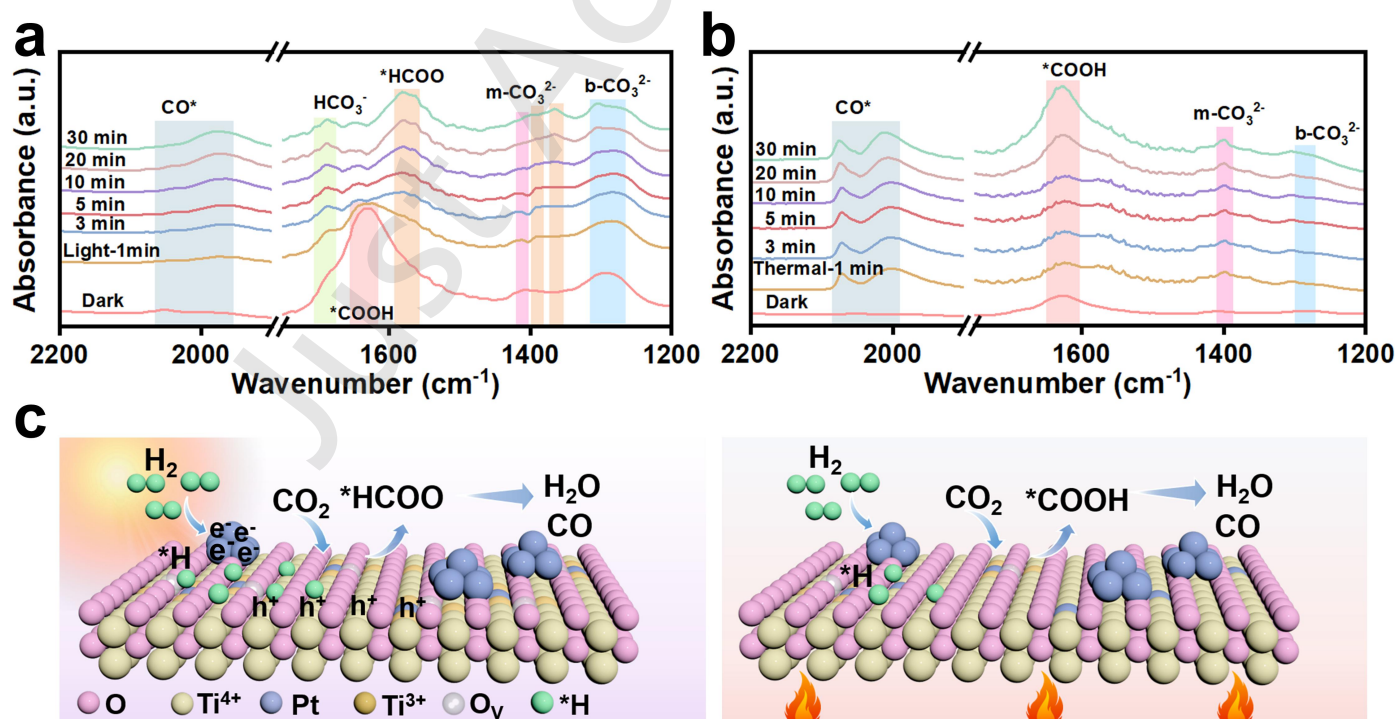


Figure 6. *in-situ* DRIFTS spectrum of Pt/TiO_2 under (a) light-driven conditions (2.5 W/cm^2 , $\sim 237\text{ }^\circ\text{C}$) and (b) thermal-driven conditions ($237\text{ }^\circ\text{C}$) ($\text{CO}_2 + \text{H}_2$ atmosphere), (c) the RWGS reaction mechanism on Pt/TiO_2 catalyst surface under light-driven and thermal-driven catalysis conditions.

3.3 The catalytic performance for light-driven RWGS

Furthermore, the practical applicability of Pt/TiO₂ catalyst in light-driven RWGS reaction is further evaluated through a series of performance tests. The effects of gas hourly space velocity (GHSV) on catalytic performance are first investigated under a constant light intensity of 2.50 W/cm². As shown in Figure 7a, as the GHSV increases from 24,000 to 480,000 mL·g⁻¹·h⁻¹, the CO production rate progressively increases while CO₂ conversion gradually decreases. Notably, at a high GHSV of 480,000 mL·g⁻¹·h⁻¹, Pt/TiO₂-LD catalyst achieves a CO production rate of 30.51 mol·g_{Pt}⁻¹·h⁻¹, with a CO₂ conversion of 9.72% and a CO selectivity of 99.12%, demonstrating the outstanding intrinsic activity. The influence of illuminated area of the catalyst on catalytic performance is also examined. With the same catalyst loading, the light intensity of 2.50 W/cm², and a GHSV of 72,000 mL·g⁻¹·h⁻¹ expanding the irradiation spot diameter from 9 mm to 18 mm results in a marked increase in CO₂ conversion from 12.72% to 28.01% (Figure 7b), highlighting the critical role of light input in driving the reaction. To investigate the photochemical contribution of light irradiation beyond the photothermal effect, the control experiments are performed using optical cut-off filters to obtain different spectral bands (UV: 200–400 nm; Vis: 420–780 nm; IR: >800 nm). The light intensity for each band is adjusted to keep the catalyst surface temperature constant at 121

°C. As shown in Figure S19, under these isothermal conditions, UV and visible light give the significantly higher CO production rates than pure thermal catalysis. This clearly demonstrates that photochemical effects participate in the reaction in addition to the photothermal effect. The operational stability of Pt/TiO₂-LD catalyst is also tested under continuous-flow light-driven RWGS conditions (2.50 W/cm², GHSV = 72,000 mL·g⁻¹·h⁻¹). As shown in Figure 7c, throughout the 144 h continuous operation, the CO selectivity remains stable above 96% and the CO₂ conversion exhibits a slight and gradual decrease from 28.49%

to 24.94%, corresponding to a deactivation rate of approximately 0.087% h⁻¹. This low deactivation rate verifies the good stability of Pt/TiO₂-LD catalyst under the tested conditions. Moreover, XRD patterns (Figure S20), XPS spectrum (Figures S21–S22) and CO-DRIFTS measurements (Figures S23) of the spent catalyst reveal no noticeable changes compared to the fresh catalyst, confirming the structural stability of the catalyst. In addition, we monitored the output power of the Xe lamp as a function of operating time (Figures S24). The light intensity gradually decreases with prolonged operation, decreasing from 2.5 W/cm² to 2.45 W/cm² after 24 h of continuous operation. This attenuation reasonably accounts for the slight decline in CO₂ conversion observed during the stability test. The performance comparison with previously reported catalysts (Figure 7d, Table S8) indicates that Pt/TiO₂-LD catalyst achieves superior CO production rate and selectivity under relatively low light intensity and catalyst surface temperature, further demonstrating its exceptional catalytic performance in the RWGS reaction [2, 3, 28, 45–48].

To evaluate the practical applicability under real-world conditions, outdoor RWGS experiments are conducted using natural sunlight as the light source in a continuous-flow reactor. Sunlight is concentrated using a Fresnel lens under ambient temperatures of approximately –20.7 °C (Figure S25). As shown in Figures 7e–f, a CO₂ conversion of 26.09% and a CO selectivity of 97.80% are achieved under the drive of natural sunlight, which are comparable to those obtained under Xe lamp irradiation with CO₂ conversion of 28.01% and CO selectivity of 97.89% (power density: 2.50 W/cm², GHSV of 72,000 mL·g⁻¹·h⁻¹), underscoring the practical application potential of the light-driven RWGS process. This efficient sunlight-driven RWGS strategy holds great promise for sustainable CO₂ conversion and carbon-neutral chemical synthesis, particularly in regions with abundant solar resources, offering a viable pathway toward renewable-energy-powered chemical production.

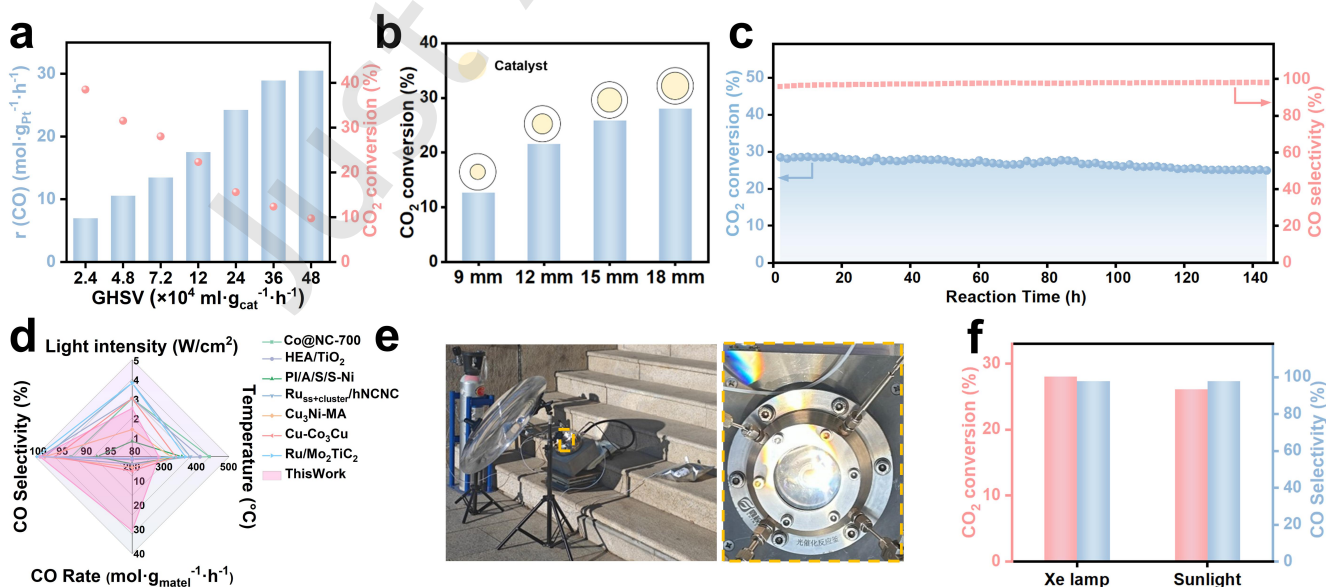


Figure 7. (a) CO production rate at different GHSV, (b) CO₂ conversion rate at different effective light exposure areas, (c) Catalytic stability test of Pt/TiO₂ catalyst, (d) Performance comparison between the Pt/TiO₂ catalyst and previously reported catalysts, (e) Actual photo of the sunlight-driven outdoor reaction system (Harbin, Heilongjiang Province, China, December 4, 2025), (f) CO₂ conversion rate and CO selectivity of Pt/TiO₂ catalyst under Xe lamp/Sunlight irradiation (GHSV = 72,000 mL·g⁻¹·h⁻¹, light intensity: 2.50 W/cm²).

4. Conclusions

In summary, we have demonstrated that light-driven charge transfer in a Pt/TiO₂ catalyst induces an enhanced hydrogen spillover effect, which optimizes the catalyst structure and reaction pathway, thus achieving the high-efficiency light-driven RWGS performance. Photoexcitation induces the spatial separation and localized accumulation of photogenerated charge carriers. Photogenerated electrons transfer to Pt, and the resulting electron-rich Pt structure facilitates H₂ dissociation, while the hole-rich TiO₂ surface promotes the migration of active H species. The synergy of electrons and holes enhances the entire hydrogen spillover process. The enhanced hydrogen spillover enables catalyst reconstruction, forming the O_v-rich Pt/TiO₂ catalyst. Combining the advantages of O_v-rich feature and enhanced hydrogen spillover, the catalyst achieves a high CO production rate of 30.51 mol·g_{Pt}⁻¹·h⁻¹ via the *HCOO pathway under the mild reaction conditions, along with superior catalytic stability, significantly outperforming the conventional thermal-driven process. More importantly, this light-driven system maintains comparable performance even under harsh outdoor conditions (−20.7 °C) using only concentrated sunlight. This work opens a new avenue for boosting RWGS performance by solar-driven catalysis, which is expected to be extendable to diverse heterogeneous hydrogenation processes.

Data availability

All data needed to support the conclusions in the paper are presented in the manuscript and the Electronic Supplementary Material. Additional data related to this paper may be requested from the corresponding author upon request.

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Declaration of competing interest

The other contributing authors report no conflict of interests in this work.

Author contribution statement

Li Fang: Writing -original draft, formal analysis, data curation, experimental design. Guiyu Huang, Yingjie Jiang, Xingyu Li and Qin Zhang: Data curation, validation, visualization. Jiayu Song, Xuanyi Hu, Yufei Liu: Formal analysis, validation. Chungui Tian: Funding acquisition, methodology, resources, writing-review & editing. Dognxu Wang and Jiancong Liu: Project administration, writing-review & editing, resources, funding acquisition, methodology, conceptualization. All the authors have approved the final manuscript.

Use of AI statement

None

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Electronic Supplementary Material

Light-enhanced hydrogen spillover on Pt/TiO₂ catalysts for efficient flow reverse water-gas shift reaction

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Characterization

Powder X-ray diffraction (XRD) measurements were performed on a SmartLab-9 kW diffractometer using Cu K α ($\lambda=1.5406$ Å) radiation with accelerating voltage of 40 kV and the current of 150 mA.

The surface morphology of the prepared samples was investigated using a Sigma-300 Zeiss scanning electron microscope (SEM).

The surface properties of the supports were obtained from N₂ adsorption-desorption isotherms at –196 °C with an ASAP 2000 Micromeritics equipment.

Transmission electron microscope (TEM), high resolution TEM (HRTEM), high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) and element mapping images were collected on a JEOL-F200 instrument with the accelerating voltage of 200 kV.

Aberration-corrected high-angle annular dark field scanning transmission electron microscopy (AC-HAADF-STEM) were obtained from a FEI TITAN Cubed Themis instrument operated at 300 kV.

X-ray photon-electron spectroscopy (XPS) measurement was performed using Thermo Fisher Scientific K-Alpha spectrophotometer with Al-K α radiation (1486.68 eV) operated at 15 kV with a filament current of 10 mA, and signals were accumulated over 3 cycles.

For in-situ irradiation XPS (ISI-XPS) analysis, the sample signals were collected under dark conditions, and then the signal collection began 5 minutes after exposure to light (full spectrum). Under both dark and light conditions, the same number of scans were performed on the sample.

Electronic paramagnetic resonance (EPR) was characterized using a Bruker EMX plus model spectrometer operated at room temperature. The Pt content of the catalyst was determined by inductively coupled plasma-optical emission spectrometry (ICP-OES, PE-Avio 200).

The UV-visible diffuse reflectance spectra (UV-vis DRS) of the samples were obtained from the UV-vis spectrophotometer test (Shimadzu UV-2550).

X-ray absorption fine structure (XAFS) measurements were measured at the BL14W1 beamline of the

Shanghai Synchrotron Radiation Facility (SSRF).

Time-Resolved Photoluminescence (TRPL) spectra were measured using the AvaSpec-ULS2048CL-EVO fiber-optic spectrometer (Avantes, Netherlands) under 375 nm excitation.

The hydrogen temperature-programmed desorption (H₂-TPD) experiments were carried out using a Tianjin Pengxiang Model 200 instrument equipped with a thermal conductivity detector (TCD). Typically, 0.10 g of in situ reduced sample was placed in a U-shaped quartz reactor, pretreated at 150 °C for 60 minutes under a N₂ flow rate of 30 mL/min, and then cooled to room temperature. Subsequently, under illuminated and dark conditions, the pre-treated sample is saturated with H₂ at a flow rate of 10 mL/min for 60 minutes, followed by purging with N₂ for 1 hour. Finally, under a nitrogen flow (27 mL/min), the sample was heated to 600 °C at a heating rate of 10 °C·min⁻¹, whilst the desorbed hydrogen was monitored.

CO adsorption diffuse reflectance Fourier transform infrared spectroscopy (CO-DRIFTS) measurements were performed using a Thermo Scientific Nicolet iS50 instrument equipped with a liquid nitrogen-cooled mercury-cadmium-telluride (MCT) detector and a high-temperature reaction cell fitted with CaF₂ and quartz windows. Prior to testing, the Pt/TiO₂-LD and Pt/TiO₂-TD samples were heated to 150 °C in a N₂ flow (20 mL/min) and held at this temperature for 1 hour. Background spectra were recorded once the reaction cell had cooled to 25 °C. Subsequently, the samples were exposed to a 10% CO/N₂ flow (20 mL/min) for 30 minutes until saturation was reached. The samples were then purged with a N₂ flow (20 mL/min) to remove gaseous CO. DRIFTS spectra were recorded at a resolution of 8 cm⁻¹ and 64 scans, and background spectra were subtracted.

For *in-situ* DRIFTS (light-driven catalysis) experiments, the Pt/TiO₂-LD sample was purged with a nitrogen flow (20 mL/min) at 150 °C for 1 hour, then heated to 237 °C and the background spectrum of the sample was recorded; the gas was subsequently switched to a gas mixture (N₂:H₂:CO₂ = 6:3:1, 20 mL/min), and the reaction cell was irradiated with a Xe lamp; the spectrum was recorded under irradiation.

For the *in-situ* DRIFTS (thermal-driven catalysis) experiments, the Pt/TiO₂-TD sample was purged with a nitrogen flow (20 mL/min) at 150 °C for 1 hour, after which the temperature was raised to 237 °C and the background spectrum of the sample was recorded. Next, the nitrogen flow was switched to a gas mixture (N₂:H₂:CO₂ = 6:3:1, 20 mL/min), and spectra were acquired to detect adsorbates on the catalyst surface.

For hydrogen spillover detection by WO₃, 1 g of WO₃ was thoroughly mixed with 0.02 g of Pt/TiO₂-Pre catalyst, or pure WO₃ was used directly, and the mixture was coated onto a glass fibre disc with a diameter of 18 mm. The catalyst-coated glass fibre was then placed in a stainless steel reactor within the reaction bed. Following heat treatment (280 °C) or light-driven treatment (2.50 W/cm², 280 °C), hydrogen gas is passed over the catalyst at a flow rate of 30 mL/min. After 10 minutes, the hydrogen flow is stopped. The reaction tube is removed from the reactor, and the color change of the powder sample is observed.

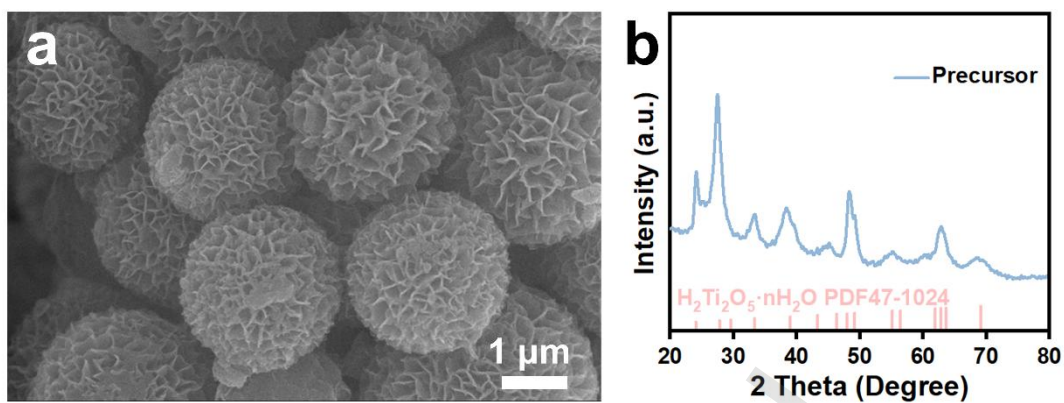


Figure S1. SEM image (a) and XRD (b) of polyhedral $\text{H}_2\text{Ti}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ spheres.

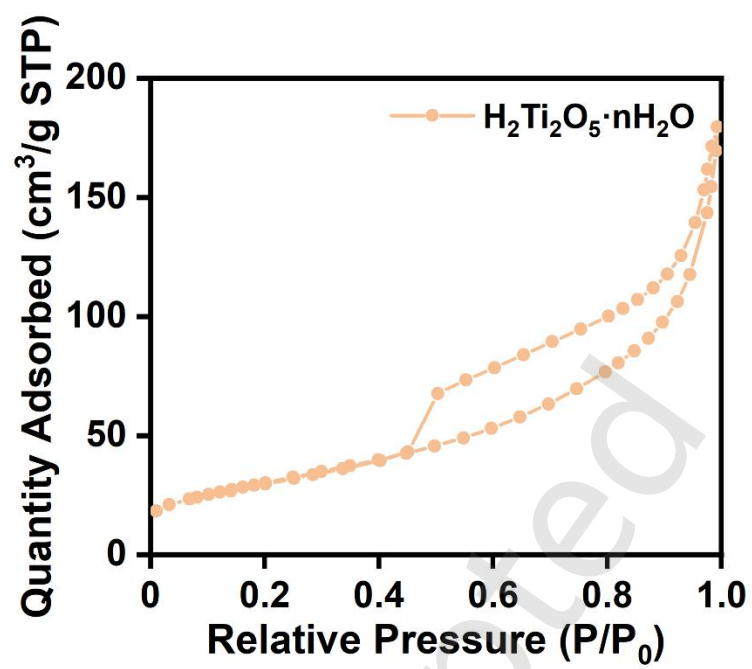


Figure S2. N_2 adsorption-desorption isotherms of the multi-edged $\text{H}_2\text{Ti}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ spheres.

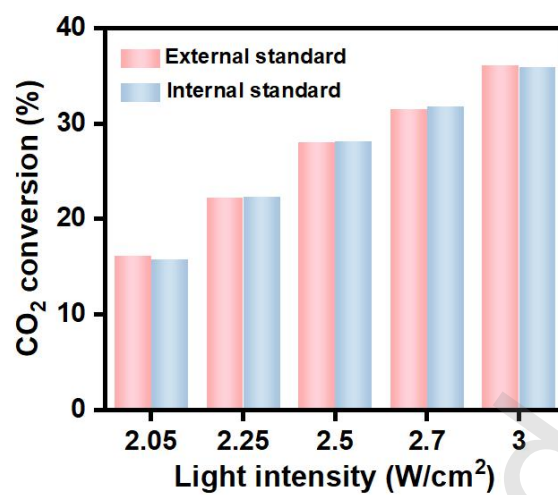


Figure S3. CO₂ conversion calculated by the internal standard method and the external standard.

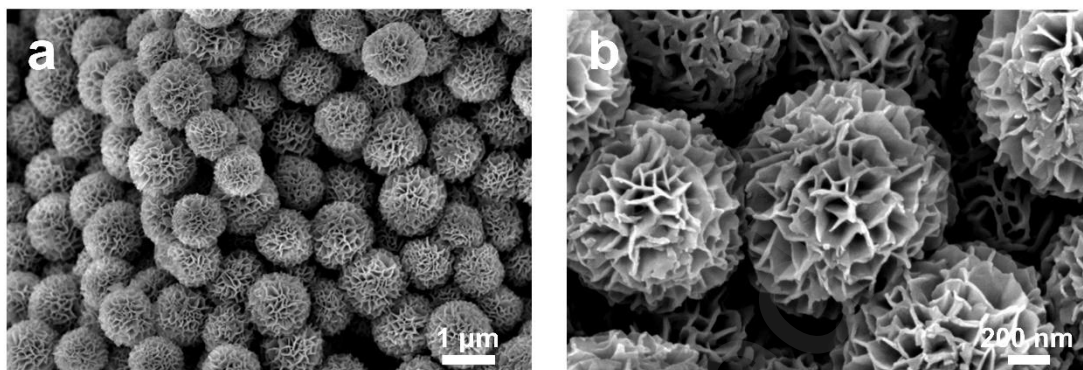


Figure S4. (a-b) SEM image of the prepared Pt/TiO₂-TD sample.

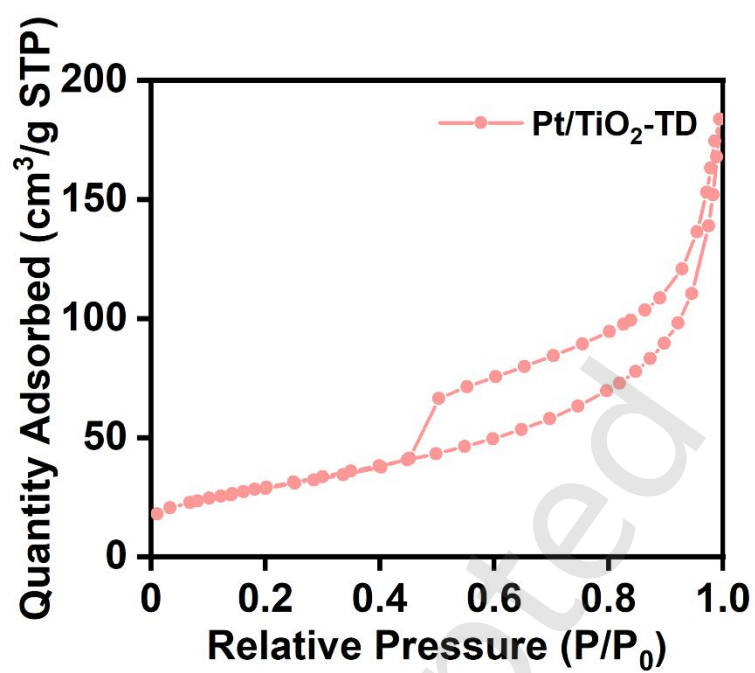


Figure S5. N₂ adsorption-desorption isotherms of Pt/TiO₂-TD.

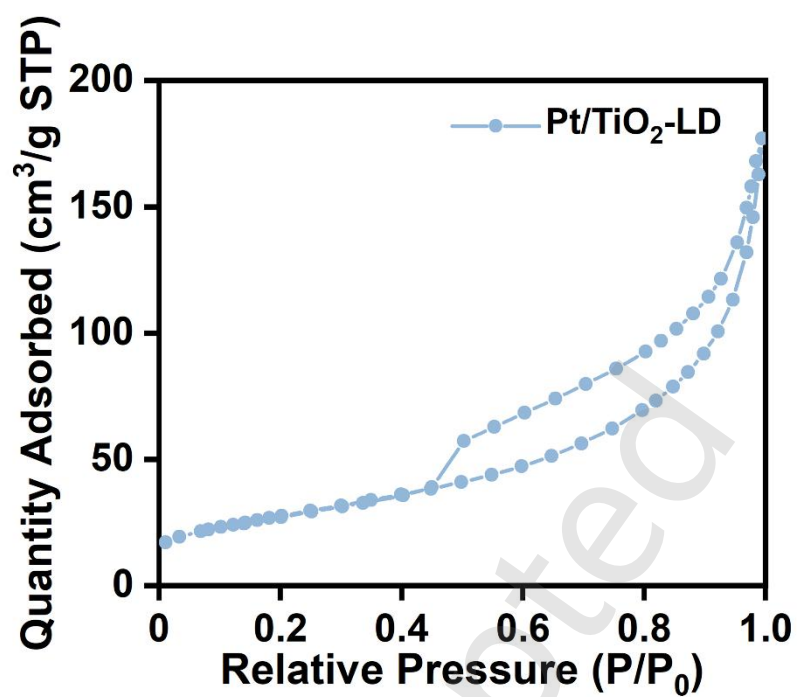


Figure S6. N₂ adsorption-desorption isotherms of Pt/TiO₂-LD.

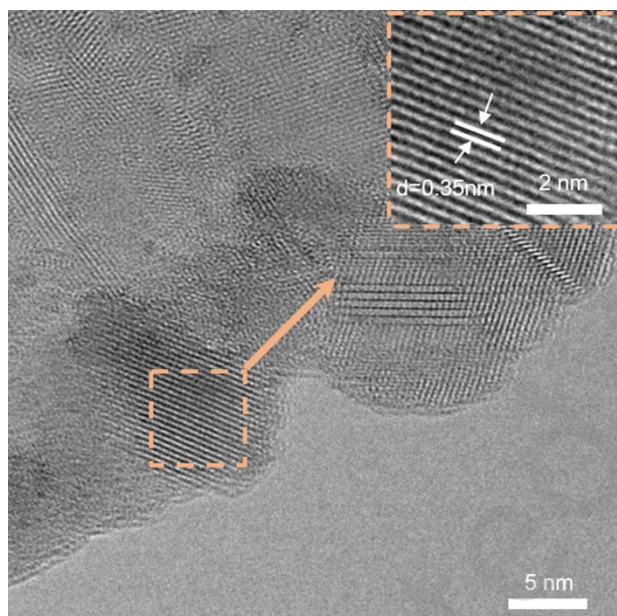


Figure S7. TEM image of the prepared Pt/TiO₂-LD sample.

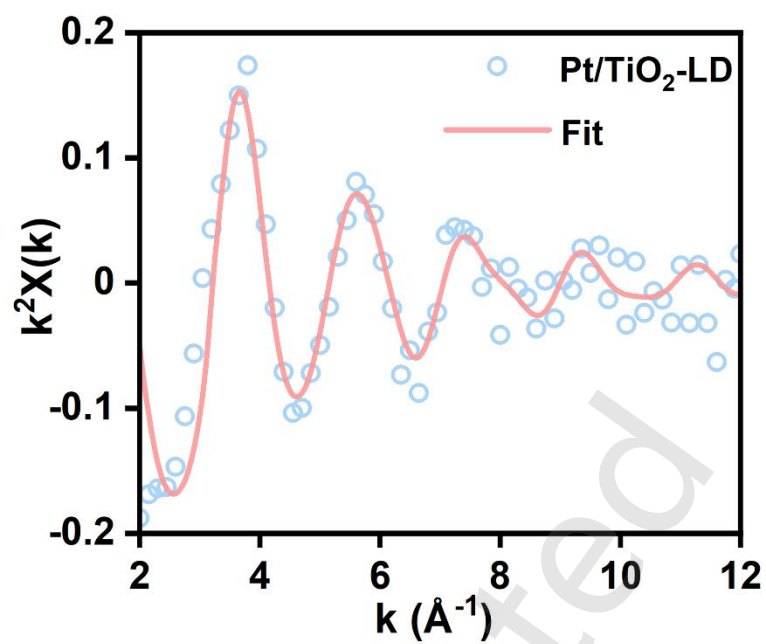


Figure S8. Fitting results of Fourier transformed k_3 -weighted EXAFS in K space of Pt/TiO₂-LD.

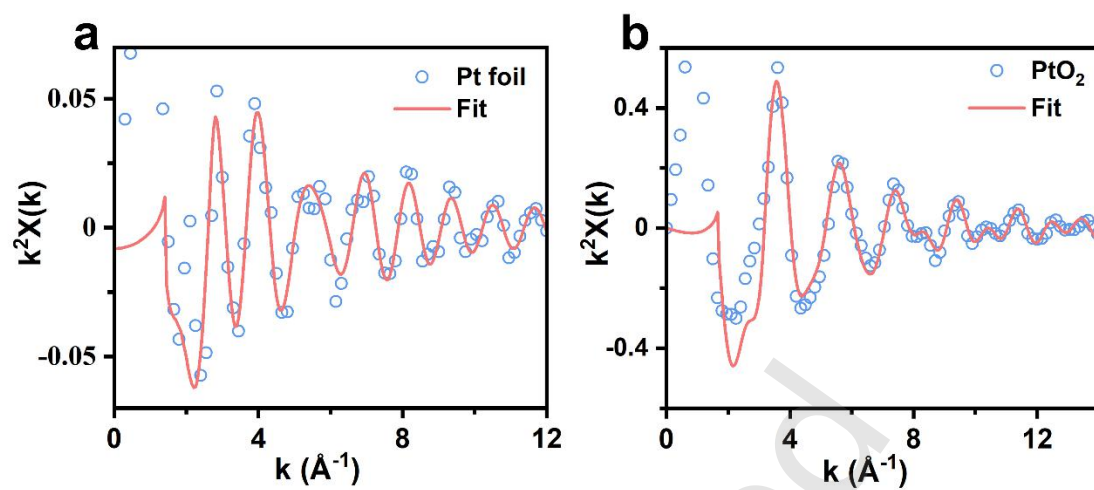


Figure S9. Fitting results of Fourier-transformed k_3 -weighted EXAFS in K space of (a) Pt foil and (b) PtO₂.

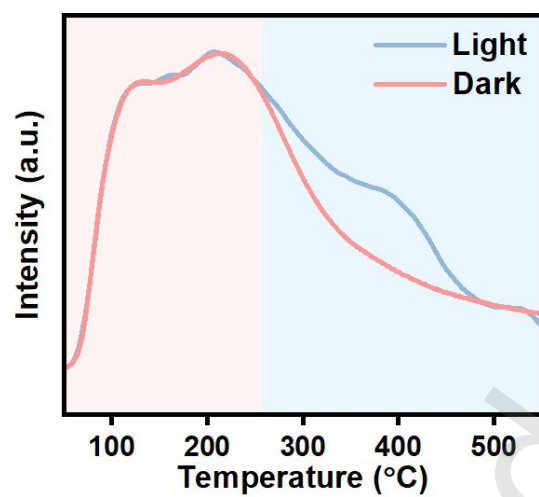


Figure S10. H₂-TPD curves of Pt/TiO₂-TD under light and dark conditions.

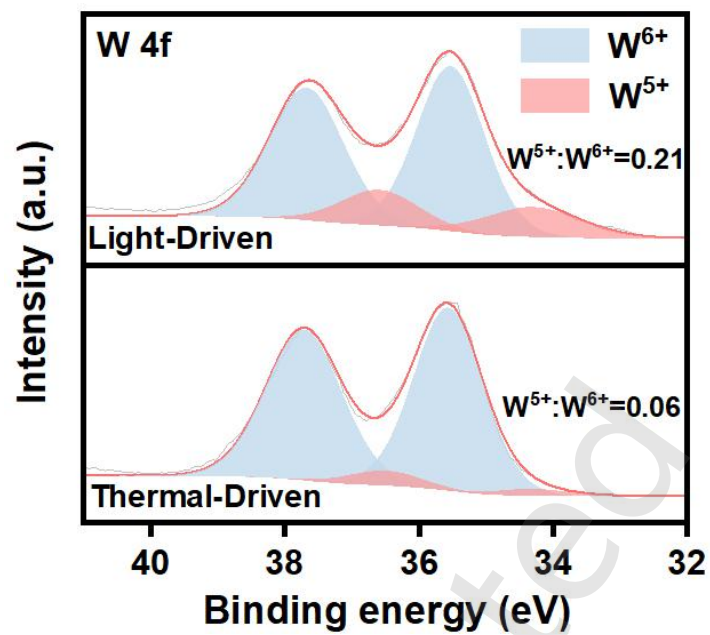


Figure S11. W 4f XPS spectra of Pt/TiO₂ under thermal-driven and light-driven conditions.

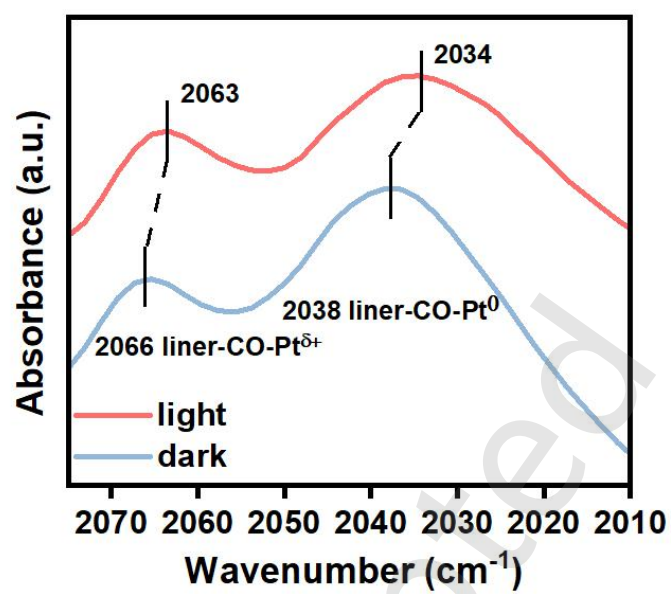


Figure S12. CO-DRIFTS results for Pt/TiO₂ under dark and light irradiation conditions.

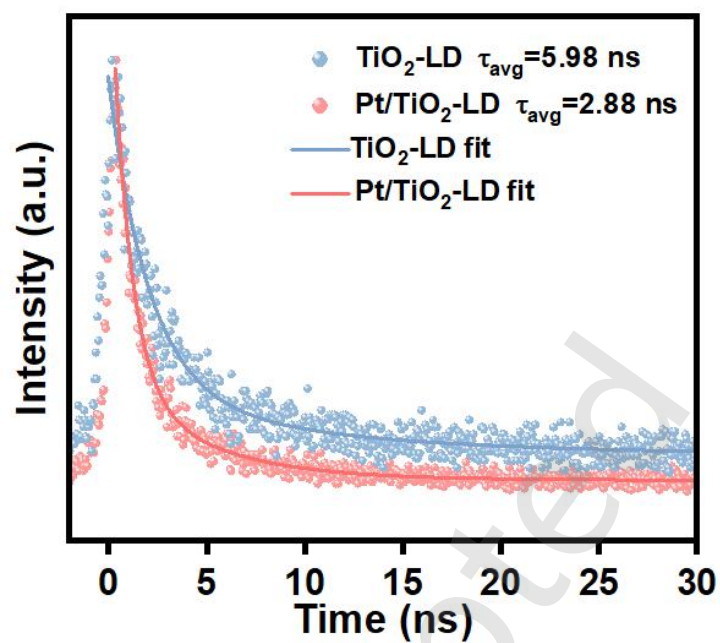


Figure S13. Time-resolved photoluminescence (TRPL) spectroscopy of $\text{TiO}_2\text{-LD}$ and $\text{Pt/TiO}_2\text{-LD}$.

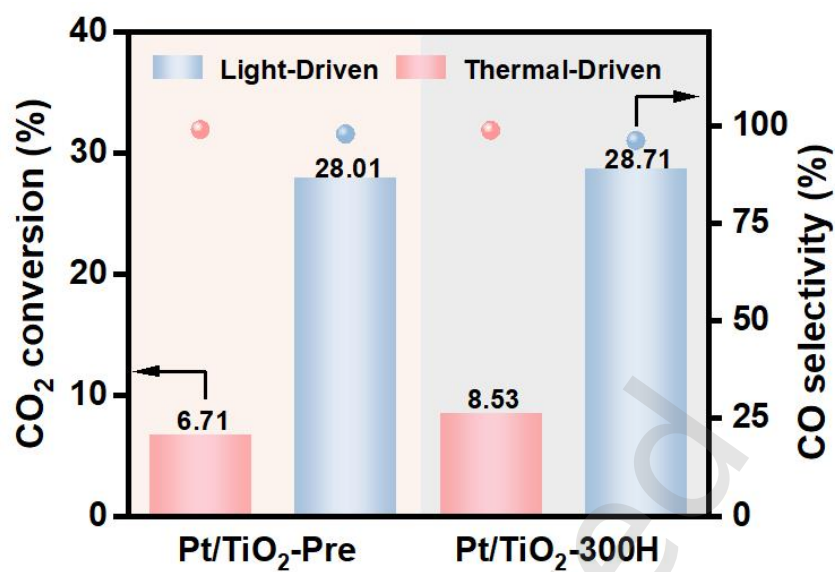


Figure S14. CO₂ conversion rates of Pt/TiO₂ catalysts under in situ reduction and pre-reduction conditions

(light intensity: 2.50 W/cm²).

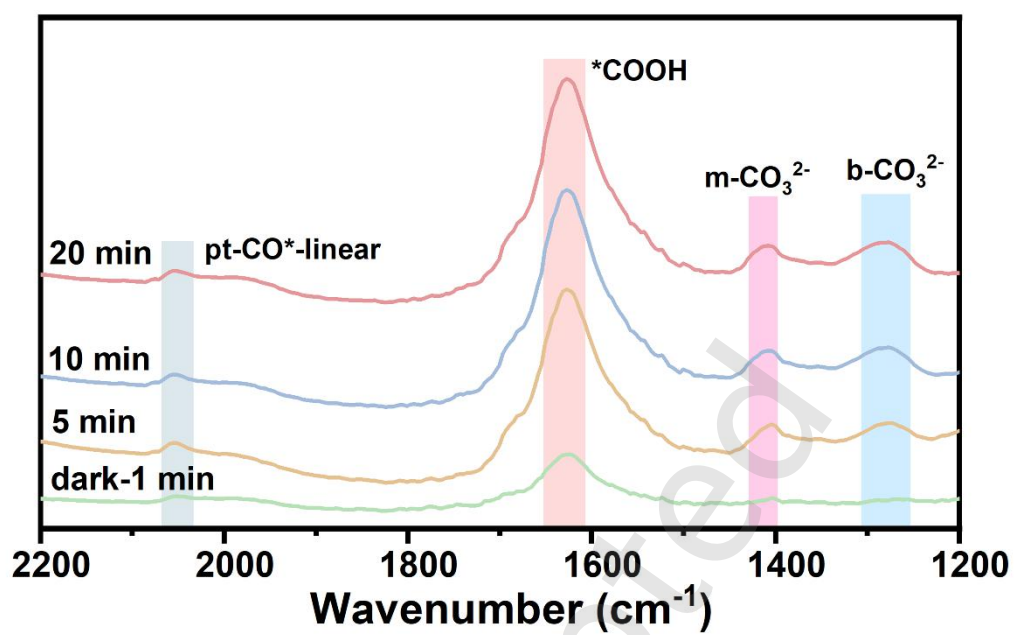


Figure S15. *In-situ* DRIFT spectroscopy of Pt/TiO₂ adsorption under CO₂ and H₂ atmospheres in the dark.



Figure S16. Photograph of the in-situ DRIFTS reactor during light driven process, showing the measured temperature of catalyst surface (via thermocouple) under illumination.

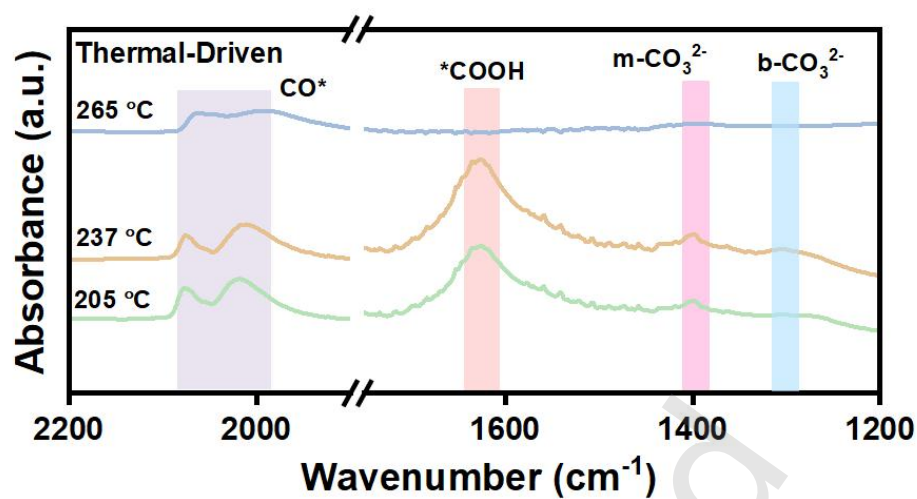


Figure S17. *In-situ* DRIFTS Spectra of Pt/TiO₂ Under Thermal Drive Conditions (at different temperatures)

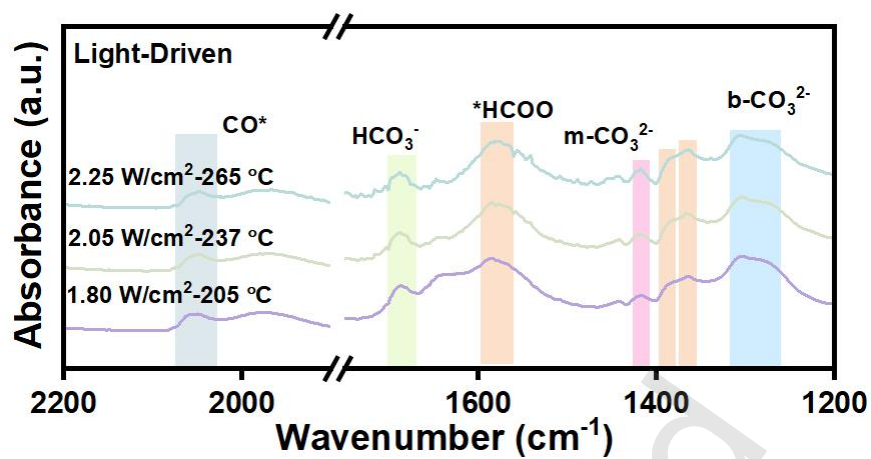


Figure S18. *In-situ* DRIFTS spectra of Pt/TiO₂ under light-driven conditions (at different light intensities)

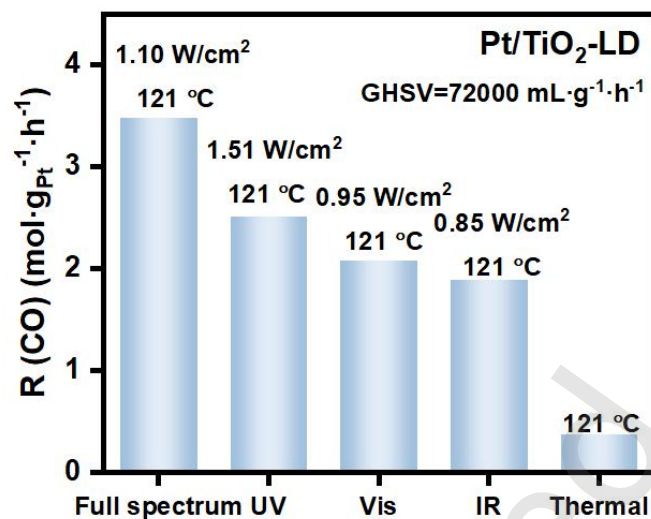


Figure S19. Light- driven RWGS performance under different spectral bands and isothermal control conditions. The same filters and reflector are used to isolate UV, Vis, IR, and full- spectrum irradiation. For each band, the light intensity is adjusted so that the catalyst surface temperature is kept constant at 121 °C.

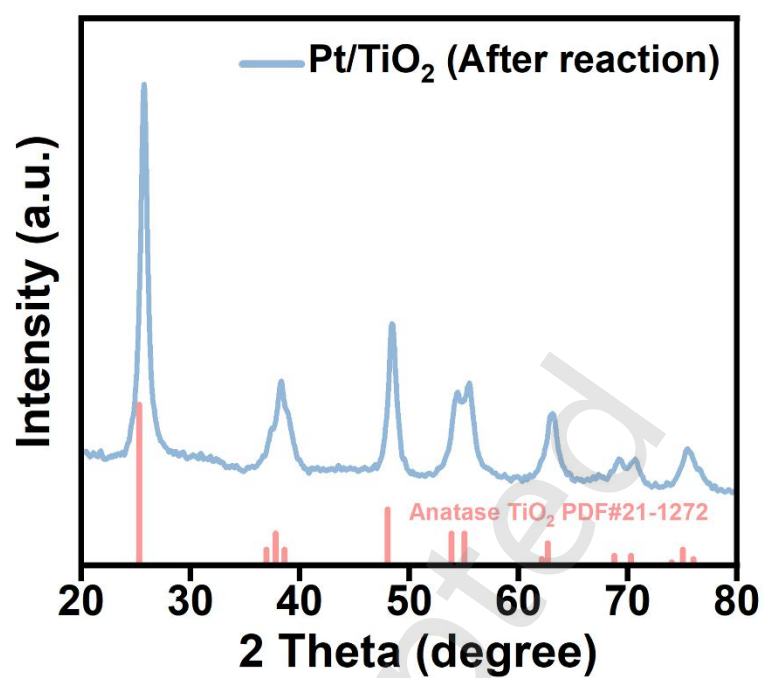


Figure S20. The XRD pattern of the Pt/TiO₂-LD catalyst after 144 hours of reaction.

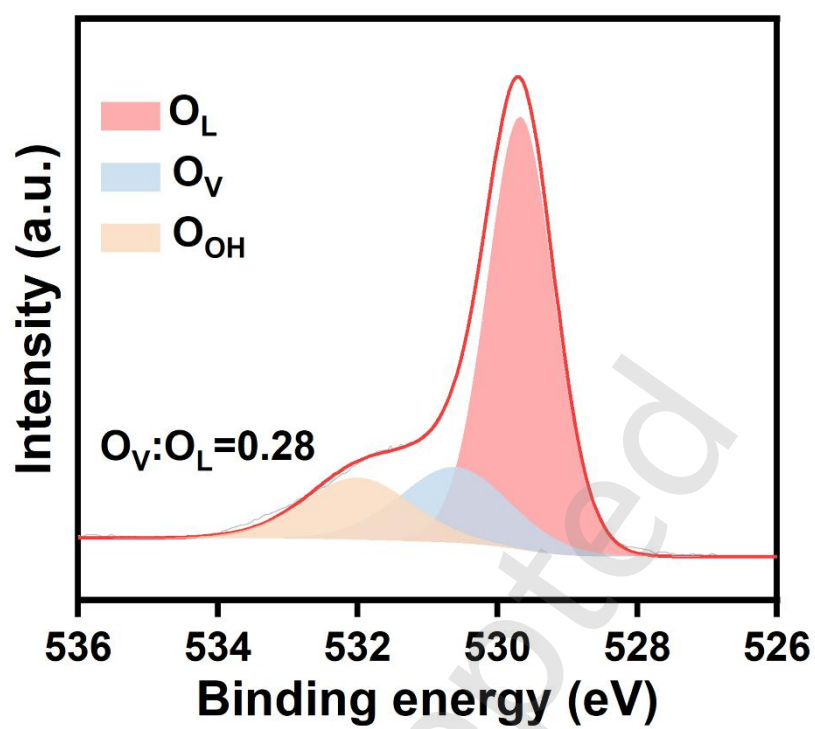


Figure S21. The O 1s XPS spectrum of the Pt/TiO₂-LD catalyst after 144 hours of reaction.

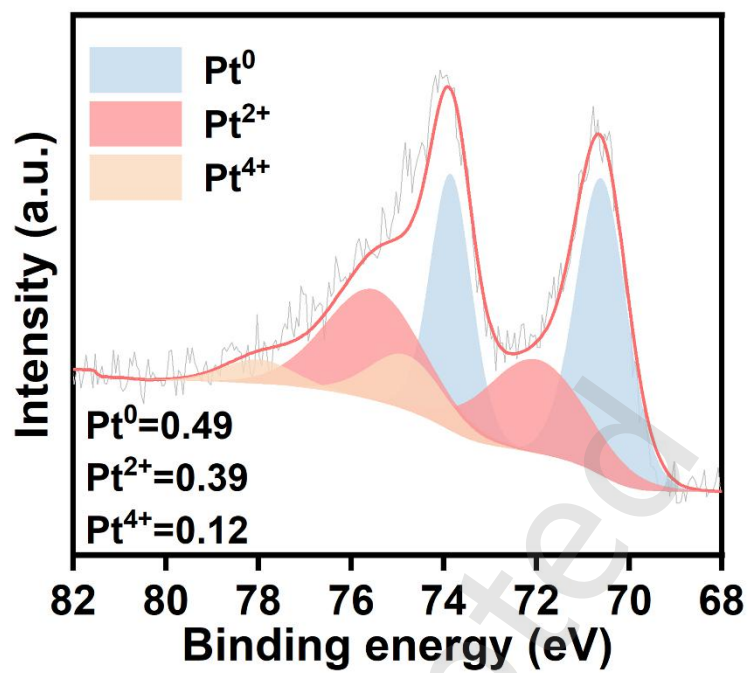


Figure S22. The Pt 4f XPS spectra of the Pt/TiO₂-LD catalyst after 144 hours of reaction.

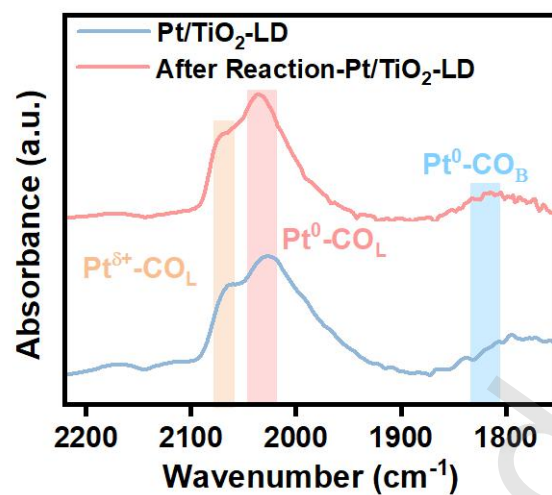


Figure S23. CO-DRIFTS spectra of the Pt/TiO₂-LD catalyst before the reaction and 144 hours after the reaction.

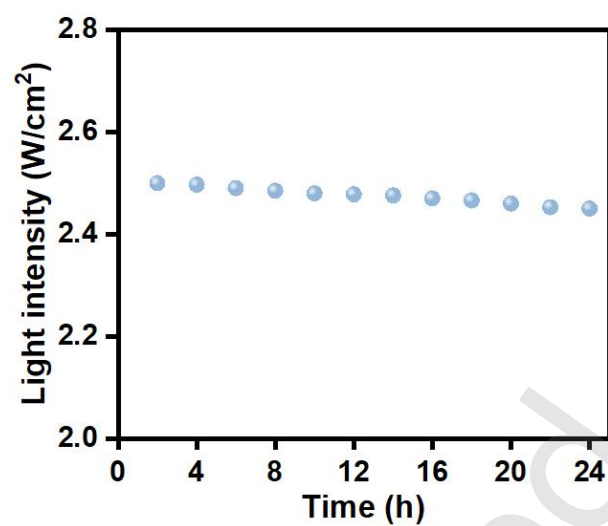


Figure S24. Decrease in Xenon lamp intensity over 24 hours.

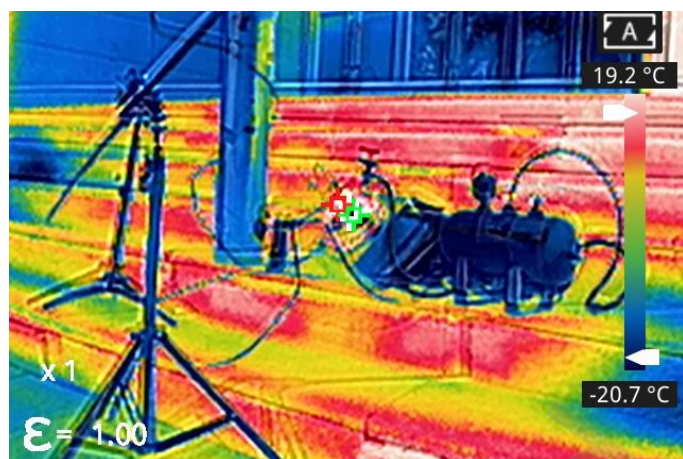


Figure S25. Infrared thermal imaging image of the reaction device.

Table S1. Textural parameters of the multi-edged $\text{H}_2\text{Ti}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ spheres, Pt/TiO₂-LD and Pt/TiO₂-TD.

Sample	S_{BET} (m^2g^{-1})
$\text{H}_2\text{Ti}_2\text{O}_5 \cdot n\text{H}_2\text{O}$	110.16
Pt/TiO ₂ -LD	100.25
Pt/TiO ₂ -TD	105.81

Table S2. CO₂ conversion based on external standard and internal standard methods.

Light intensity (W/cm ²)	CO ₂ conversion (%) (external std.)	CO conversion (%) (inner std.)
2.05	16.18	15.82
2.25	22.22	22.33
2.50	28.01	28.15
2.70	31.49	31.75
3.00	36.04	35.85

Table S3. Carbon balance results under different reaction conditions.

Light intensity (W/cm ²)	CO ₂ (out) (%)	CO (out) (%)	CH ₄ (out) (%)	Carbon balance (%)
2.05	20.79	3.89	0.12	99.20
2.25	19.32	5.24	0.15	98.84
2.5	17.18	7.07	0.36	98.44
2.7	16.63	7.59	0.46	98.72
3.0	15.75	8.27	0.55	98.28

Table S4. Elemental composition and platinum loading of the Pt/TiO₂-LD and Pt/TiO₂-TD catalysts.

Catalyst	Elemental compositions	Pt loading (wt %)
Pt/TiO ₂ -LD	Pt, Ti, O	1.67
Pt/TiO ₂ -TD	Pt, Ti, O	1.73

Table S5. EXAFS fitting parameters at the Pt L₃-edge for various samples.

Sample	Shell	<i>N</i>	<i>R</i> (Å)	$\sigma^2(10^{-3} \text{ \AA}^2)$	ΔE_0 (eV)	<i>R</i> factor
Pt-foil	Pt-Pt	12	2.76	4.64	7.55	0.0014
	Pt-O	5.71	2.01	2.81		
PtO ₂	Pt-Pt	7.75	3.11	4.19	9.7	0.0211
	Pt-O	6.64	3.65	2.04		
	Pt-O	1.99	2.02	2.47	9.8	0.0219
	Pt-Pt	1.50	3.14	7.99		

N: the coordination number. *R*: the interatomic distance (bond length from center atom to coordination atom).

σ^2 : Debye-Waller factor to evaluate thermal and static disorder. ΔE_0 : inner potential correction. **amp**: the

amplitude reduction factor (amp = 0.830 was determined by fitting EXAFS spectrum of Pt foil). **R factor**:

the change of the interatomic distance relative to the initial length.

Table S6. Light-Dark XPS Element Content Analysis Table.

Element	Elemental Proportion (%)	
	Light	Dark
Ti ³⁺ (%)	5.88	4.62
Ti ⁴⁺ (%)	94	96
Ti ³⁺ /Ti ⁴⁺	0.06	0.05
Pt ⁰ (%)	48	48
Pt ²⁺ (%)	40	40
Pt ⁴⁺ (%)	12	12
O _L (%)	74	73
O _V (%)	20	20
O _{OH} (%)	5.74	7.41
O _V /O _L	0.27	0.27

Table S7. Kinetic parameters derived from the Time-resolved photoluminescence (TRPL) spectroscopy.

Sample	τ_1 (ns)	A_1	τ_1 (ns)	A_2	τ_{avg} (ns)
TiO ₂ -LD	2.05416	0.71363	9.99511	0.14344	5.98
Pt/TiO ₂ -LD	0.92599	1.03689	4.56859	0.24286	2.88

Table S8. Performance Comparison of Photothermal Catalysts.

Catalyst	Light intensity (W/cm ²)	Rate (mol·g _{matel} ⁻¹ ·h ⁻¹)	H ₂ :CO ₂	T (°C)	CO ₂ CON (%)	Select (%)	Ref
Cu ₃ Ni-MA	1.4	4.402	1	320	N/A	>98	[2]
Co@NC-700	3	0.75	1	439	60	92.6	[48]
PI/A/S/S-Ni	0.8	2.94	5	354.2	N/A	87.3	[45]
Ru _{ss+cluster} /hNC NC	3.8	3.10	1	380	N/A	>98	[3]
HEA/TiO ₂	3.0	1.23	1	410	N/A	>99	[28]
Cu-Co ₃ Cu	3	5.94	1	335	N/A	95.8	[47].
Ru/Mo ₂ TiC ₂	3.8	0.678	1	365	2	99.7	[46]
Pt/TiO ₂ -LD	2.5	30.51	3	283	9.72	99.1	This Work