

# Highly selective CO<sub>2</sub>-to-CH<sub>4</sub> conversion via multisun-assisted photocatalysis enabled by dual cocatalyst interfaces

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## ABSTRACT

Photocatalytic CO<sub>2</sub> reduction to value-added chemicals is limited by inefficient charge transfer and sluggish multielectron kinetics. Here, we develop a TiO<sub>2</sub> (P25) based ternary system incorporating Pt NPs and 1T-dominant MoSe<sub>2</sub> NSs as dual cocatalysts (i.e., Pt/TiO<sub>2</sub>-MoSe<sub>2</sub>) to direct charge flow and reaction pathways. This Pt/TM architecture accelerates charge separation and provides highly active sites for CO<sub>2</sub> activation. The optimized Pt<sub>1.5</sub>%-TiO<sub>2</sub>-MoSe<sub>2</sub> exhibits a CH<sub>4</sub> evolution rate of 17.81 μmol g<sup>-1</sup> under 5-sun illumination with ≈ 98% selectivity in the gas phase, achieving a 65-fold enhancement over TiO<sub>2</sub> (P25). Under multi-sun irradiation, increased photon flux boosts activity, indicating the critical role of charge carrier density, and facilitates rapid CH<sub>4</sub> desorption, thereby overcoming the activity-selectivity trade-off. The coexistence of static interfacial charge redistribution and dynamic photoinduced electron transfer, validated by experiment (XPS, XAS) and Density Functional Theory (DFT) quantum mechanics (QM) calculations, ensures the retention of the active 1T-MoSe<sub>2</sub> phase and establishes an efficient TiO<sub>2</sub> → MoSe<sub>2</sub> → Pt charge-funneling highway. In situ DRIFTS, combined with simulated infrared spectra (DFT), identifies a \*CHO-dominated pathway for the conversion (\*CO → \*CHO → \*CHOH → \*CH<sub>2</sub>OH → \*CH<sub>2</sub> → \*CH<sub>3</sub> → CH<sub>4</sub>), and isotopic labeling confirms the CO<sub>2</sub>-to-CH<sub>4</sub> formation. DFT results further support the cascade charge transfer and reduced energy barriers enabled by the dual cocatalyst system.

## 1. Introduction

Solar-driven conversion of low-concentration CO<sub>2</sub> into useful chemicals and fuels offers a way to turn even dilute carbon sources into renewable energy carriers [1–3]. Yet, this remains challenging due to limited CO<sub>2</sub> availability and slow reaction kinetics [4–6]. TiO<sub>2</sub> stands out as one of the best photocatalysts due to its cost-effectiveness, sustainability, and photostability; however, its usefulness in CO<sub>2</sub> reduction is curtailed by a wide bandgap, rapid charge recombination, and limited understanding of its surface catalytic activity [7]. Extensive research has explored different cocatalysts to improve the performance of TiO<sub>2</sub>, focusing on metal nanoparticles (NPs) such as Pt, Ag, Au, Pd, and Cu, as well as their bimetallic combinations. Fewer studies have investigated

non-metal cocatalysts [8]. Most work highlights the role of metal NPs in enhancing charge separation and catalytic activity.

Two-dimensional transition metal dichalcogenides (TMDs) such as MoS<sub>2</sub> and MoSe<sub>2</sub> have emerged as promising nonprecious materials owing to their unique optical and electronic properties [9]. MoSe<sub>2</sub> has gained attention for energy applications due to its high electrical conductivity, and its easy-to-form Se–Mo–Se layered structure [10]. MoSe<sub>2</sub> has been explored as a cocatalyst for photocatalytic H<sub>2</sub> production, showing potential to replace Pt because of its favorable Se–H<sub>ads</sub> bond energy (273 kJ/mol) compared to Pt–H (251 kJ/mol) [11,12]. DFT studies by Nørskov et al. also indicate its capability for CO<sub>2</sub> reduction [13]. With a narrow band gap (1.1–1.8 eV), MoSe<sub>2</sub> enhances visible-light absorption and facilitates CO<sub>2</sub> photoreduction. Previous

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studies employed MoSe<sub>2</sub> in a heterostructure formation with another semiconductor for photocatalytic CO<sub>2</sub> reduction in a liquid phase using triethanolamine (TEOA) as a sacrificial agent [14,15]. Similarly, MoSe<sub>2</sub> with 1T-phase dominance can also be used as a cocatalyst for photocatalytic CO<sub>2</sub> reduction [16], depending on the synthesis approach of the catalyst. The quantum-confinement effect enables an indirect-to-direct band-gap transition in bulk-to-nanolayered MoSe<sub>2</sub>. Therefore, exfoliation of bulk MoSe<sub>2</sub> into multi-layered structures can be possible, in which the weakly bonded two-dimensional (2D) atomic layers (i.e., nanosheets) can be separated [17]. These multilayers can be combined with other semiconductors to make them useful materials for photocatalytic CO<sub>2</sub> reduction reactions. Most MoSe<sub>2</sub>-based photocatalysts reported to date are binary composites but still fall short of fully exploiting this material's synergistic potential. Thus, further exploration of their properties and CO<sub>2</sub> reduction performance is highly desirable. Constructing a ternary hybrid architecture by integrating additional active components offers a promising route to enhanced efficiency. Anchoring Pt NPs as co-catalysts can significantly boost activity through their localized surface plasmon resonance (LSPR) effect, which broadens visible-light absorption and improves charge separation [18]. In addition, they provide highly active adsorption sites, which are crucial for gas-phase CO<sub>2</sub> reduction, where efficient CO<sub>2</sub> activation is essential [19].

Based on these insights, we designed a Pt/TiO<sub>2</sub>-MoSe<sub>2</sub> (Pt/TM) ternary photocatalyst to improve low-concentration CO<sub>2</sub> photoreduction. Although MoSe<sub>2</sub> alone shows limited activity, integrating Pt NPs and MoSe<sub>2</sub> nanosheets on TiO<sub>2</sub> creates a dual co-catalyst system that enhances charge separation and CO<sub>2</sub> activation. Pt acts as an electron trap and multi-electron transfer center, while MoSe<sub>2</sub> edge sites and Se vacancies provide Lewis basic sites for strong CO<sub>2</sub> adsorption and activation, enabling efficient and selective CO<sub>2</sub> reduction. The Pt<sub>1.5%</sub>-TM catalyst exhibited superior CO<sub>2</sub>-to-CH<sub>4</sub> conversion activity under 5-sun illumination, with  $\approx$  98% CH<sub>4</sub> selectivity with a trace of C<sub>2</sub>H<sub>6</sub>, and 24-hour stability. This enhanced performance under multi-sun irradiation stems from increased photon flux, which generates more reactive electrons and holes, thereby accelerating charge utilization, CO<sub>2</sub> activation, and CH<sub>4</sub> desorption. In situ EXAFS, TRPL, operando spectroscopies, isotopic labeling, and DFT calculations revealed the charge-transfer dynamics and the CO<sub>2</sub> reduction pathway responsible for enhanced performance.

## 2. Experimental section

### 2.1. Exfoliation of MoSe<sub>2</sub>

50 mg MoSe<sub>2</sub> was dispersed in a MeOH + DI H<sub>2</sub>O mixture (15 + 35 mL) and sonicated for 2 h at ambient temperature. Then, the solution was collected through centrifugation at 3000 rpm for 7 min. The exfoliated solution was stored in a refrigerator to synthesize the TiO<sub>2</sub>-MoSe<sub>2</sub> samples.

### 2.2. Synthesis of TiO<sub>2</sub>-MoSe<sub>2</sub> (TM)

200 mg of P25 (Degussa) was mixed with X mL of exfoliated MoSe<sub>2</sub> solution and 15 mL of DI water, and sonicated for 20 min. Then the mixture was stirred for 4 h at ambient conditions, centrifuged at 15000 rpm for 10 min, and dried at 90 °C in a vacuum oven for 12 h. The solid powder was vacuum annealed in a furnace connected to a vacuum pump at 200 °C for 2 h. After the furnace had cooled naturally, the TM was collected. TM<sub>x%</sub> with varying MoSe<sub>2</sub> amounts (X = 5, 10, 15, 20, and 30 mL) compared to P25 were synthesized. The mass loadings of MoSe<sub>2</sub> were determined to be 0.113, 0.235, 0.443, 0.562, and 0.755% for TM5, TM10, TM15, TM20, and TM30, respectively (detailed elemental profiles are provided in Table S1).

### 2.3. Synthesis of Pt/TiO<sub>2</sub>-MoSe<sub>2</sub> (Pt-TM)

100 mg TM was dispersed in a certain amount of DI-H<sub>2</sub>O, methanol (5 mL), and different amounts (y%) of Pt precursor solutions (i.e., H<sub>2</sub>PtCl<sub>6</sub>). The reaction mixture was stirred in the dark for 1 h, followed by irradiation under a 300 W Xe lamp for 2 h with mild stirring. The Pt-deposited TM composite was recovered by centrifugation and copiously washed with DI water, diluted H<sub>2</sub>O<sub>2</sub>, and again with DI water. Finally, the sample was dried at 90 °C in a vacuum oven for 12 h. The varied amount of Pt content in TM was prepared and named Pt<sub>y%</sub>-TM, where 'y' is the wt% of Pt (y% = 0.5, 1.0, 1.5, 2.0, and 2.5%).

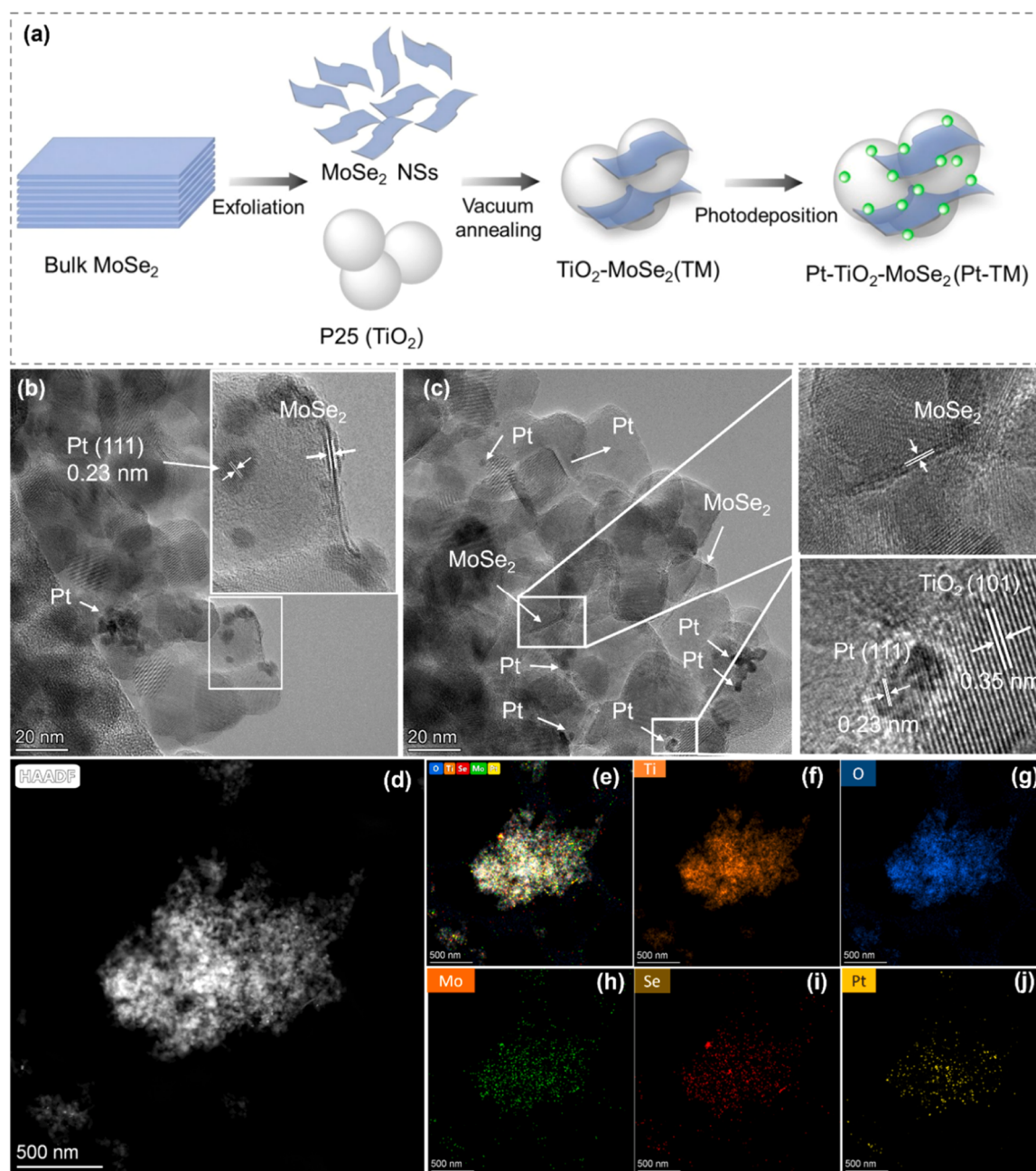
## 3. Results and discussion

### 3.1. Morphology and surface coordination chemistry

The optimized TiO<sub>2</sub>-MoSe<sub>2</sub> (TM) was first prepared, followed by Pt deposition (Fig. 1a). Among these, Pt<sub>1.5%</sub>-TM exhibited the highest CO<sub>2</sub> reduction activity; therefore, P25, TM, and Pt<sub>1.5%</sub>-TM were selected for further characterization. Morphological features were analyzed by field emission scanning electron microscopy (FE-SEM) and high-resolution transmission electron microscopy (HR-TEM) (Figs. 1b-j and S1-S4). Bulk MoSe<sub>2</sub> (before exfoliation) exhibited a sandwich-like morphology with stacked and closely packed sheets extending to several micrometers (Fig. S1). After exfoliation, MoSe<sub>2</sub> nanosheets (NSs) were integrated with P25 (Fig. S2). A similar morphology was observed for Pt<sub>1.5%</sub>-TM (Fig. S3). Energy-dispersive spectroscopy (EDS) confirmed the presence of Ti, O, Mo, and Se, which was further supported by elemental mapping (Figs. S3c-h). In the Pt<sub>1.5%</sub>-TM composite, HR-TEM images reveal MoSe<sub>2</sub> NSs entangled with TiO<sub>2</sub> edges, while finely distributed Pt NPs with spherical morphology are anchored on both TiO<sub>2</sub> and MoSe<sub>2</sub> surfaces (Figs. 1b, c, and S4). The lattice fringes with interplanar spacings of 0.35 nm and 0.23 nm correspond to the (101) plane of anatase TiO<sub>2</sub> and the (111) plane of metallic Pt, respectively. Statistical analysis based on HR-TEM images shows that the Pt NPs possess an average particle size of 5.6 nm (Fig. S4f). High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images (Fig. 1d) further confirmed the presence of Pt on the TiO<sub>2</sub>-MoSe<sub>2</sub> heterostructure, indicating close interfacial contact. EDS elemental mapping revealed the distribution of Ti, O, Mo, Se, and Pt throughout the nanostructure (Fig. 1e-j). The measured elemental contents from inductively coupled plasma optical emission spectroscopy (ICP-OES) in the Pt<sub>1.5%</sub>-TM composite are 1.21 wt % Pt, 0.15 wt % Mo, and 0.28 wt % Se.

X-ray diffraction (XRD) patterns of exfoliated MoSe<sub>2</sub> nanosheets show the characteristic features of a mixed 2H/1T phase transition (Fig. S5). The exfoliation of MoSe<sub>2</sub> was confirmed by the dominance of the (002) basal plane reflection and the emergence of characteristic 1T-phase peaks at 32.9° and 61.7° [20,21]. This 1T feature of MoSe<sub>2</sub> provides the increased conductivity for CO<sub>2</sub> photoreduction. In the XRD of composites, all the peaks correspond to TiO<sub>2</sub> (Fig. 2a). MoSe<sub>2</sub> or Pt introduction did not change the diffraction pattern of TiO<sub>2</sub> due to their low concentration and low diffraction intensity. Raman was analyzed to confirm the sample's chemical composition and surface changes after composite formation (Fig. 2b, c). The Raman spectra display characteristic anatase TiO<sub>2</sub> vibrational modes, with five Raman bands (i.e., 2Eg + B1g + A1g + Eg) (Fig. 2b). The strongest Eg band was observed at 149.2 cm<sup>-1</sup>. In the case of the TM, a slight shift of the Eg band towards lower wavenumbers, from 149.2 to 146.07 cm<sup>-1</sup>, was observed. Such a shift might be caused by charge transfer between TiO<sub>2</sub> and MoSe<sub>2</sub>, implying that the two are nearby [22,23]. However, when the Pt NPs were deposited on TM, the Eg peak was blue-shifted from 146.07 to 153.81 cm<sup>-1</sup>, ascribed to the surface-enhanced Raman scattering effect due to the successful deposition of Pt NPs on TM [24]. These results indicate that MoSe<sub>2</sub> and Pt are deposited on the P25 to form the Pt-TM composite.

X-ray photoelectron spectroscopy (XPS) was recorded to examine the

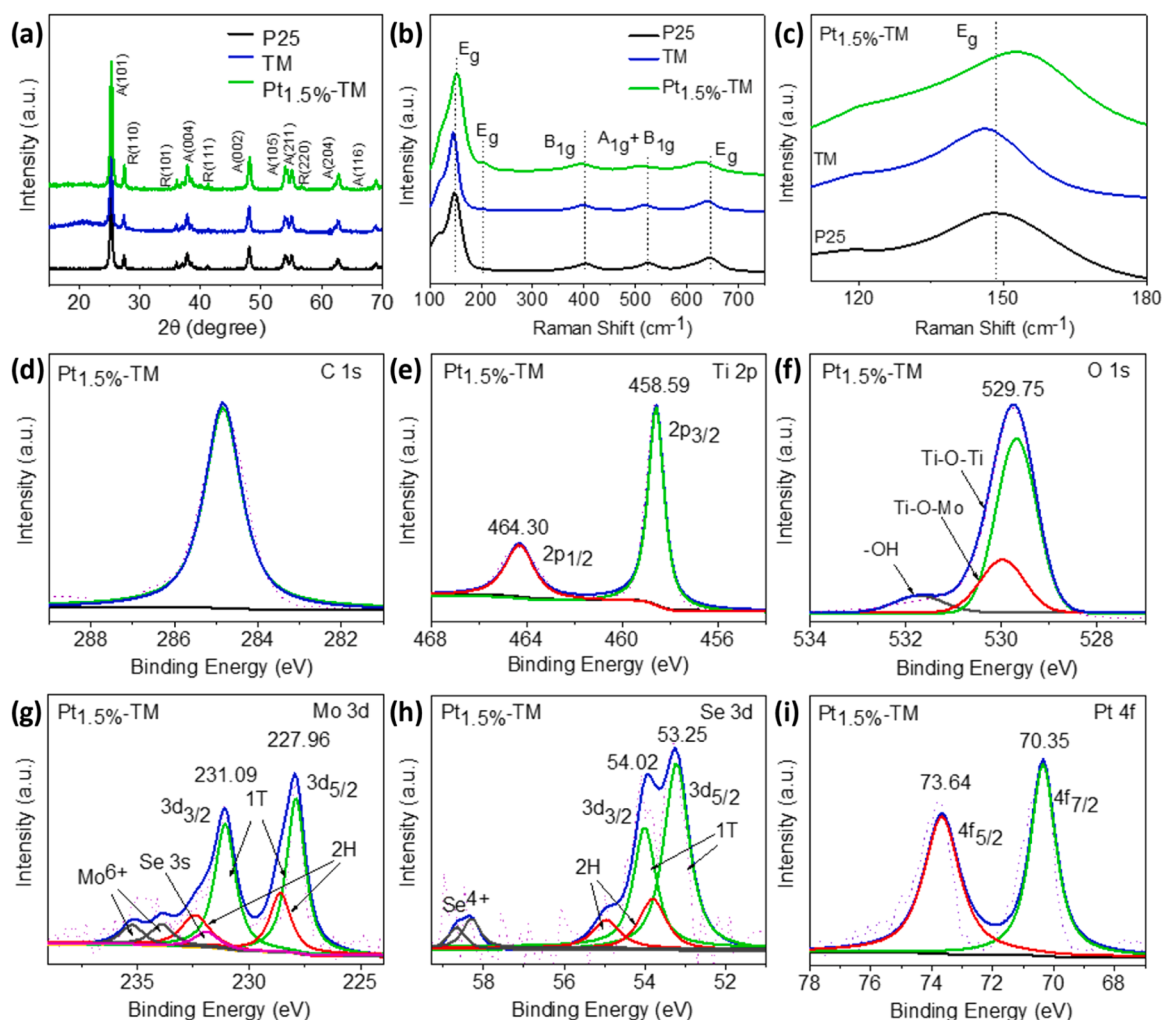


**Fig. 1.** (a) Schematic of synthesis of Pt-TM photocatalyst, (b-c) HR-TEM, (d) HAADF, and (e) elemental mapping of Pt<sub>1.5%</sub>-TM for (f) Ti, (g) O, (h) Mo, (i) Se, and (j) Pt elements.

surface information of the MoSe<sub>2</sub>, exfoliated MoSe<sub>2</sub>, P25, TM, and Pt<sub>1.5%</sub>-TM (Figs. S6-S9 and 2d-i). All spectra were calibrated using the adventitious C 1 s peak. XPS analysis of the initial bulk powder and the liquid-phase exfoliated nanosheets reveals the electronic impact of the exfoliation process (Fig. S7). The bulk MoSe<sub>2</sub> exhibits characteristic Mo 3d<sub>5/2</sub> and Mo 3d<sub>3/2</sub> doublets at 229.36 eV and 232.46 eV, respectively, corresponding to the stable 2H phase. Following exfoliation, these peaks shift to 229.00 eV and 232.14 eV. A similar shift in Se 3d was observed in MoSe<sub>2</sub> and exfoliated MoSe<sub>2</sub>. While deconvolution shows a minor contribution from the metallic 1T phase induced by high-energy sonication, the 2H phase remains dominant [20,21]. This is attributed to the metastable nature of the 1T configuration; without a stabilizing electronic donor (e.g., TiO<sub>2</sub>) or high-energy surface, the nanosheets undergo structural relaxation and restacking back into the thermodynamically stable 2H state during solvent evaporation [25]. While in the TM, the Mo

3d and Se 3d peaks undergo a downshift to ~227.98/231.14 eV and ~53.55/54.33, representing a complete 1T-dominant state (Figs. S8d, e). This stabilization is driven by the strong metal-support interaction (SMSI) at the heterojunction. The TiO<sub>2</sub> support acts as a persistent electron reservoir, injecting charge into the MoSe<sub>2</sub> lattice via interfacial Ti-O-Mo linkages (Figs. S8b, c). This continuous electronic enrichment effectively locks the MoSe<sub>2</sub> in the metallic 1T phase, preventing the structural reversion observed on inert substrates. Consequently, the TiO<sub>2</sub> does not merely serve as a physical scaffold but functions as a critical electronic stabilizer, ensuring the retention of the high conductivity 1T phase for enhanced catalytic performance.

In Pt<sub>1.5%</sub>-TM, the Ti 2p core-level spectrum showed two peaks at 458.63 and 464.30 eV, assigned to Ti 2p<sub>3/2</sub> and Ti 2p<sub>1/2</sub>, respectively (Fig. 2e) [26,27]. The distance between the 2p<sub>3/2</sub> and 2p<sub>1/2</sub> core levels is 5.8 eV, suggesting Ti<sup>4+</sup> in TiO<sub>2</sub> [28,29]. For the O 1 s spectrum, peaks at

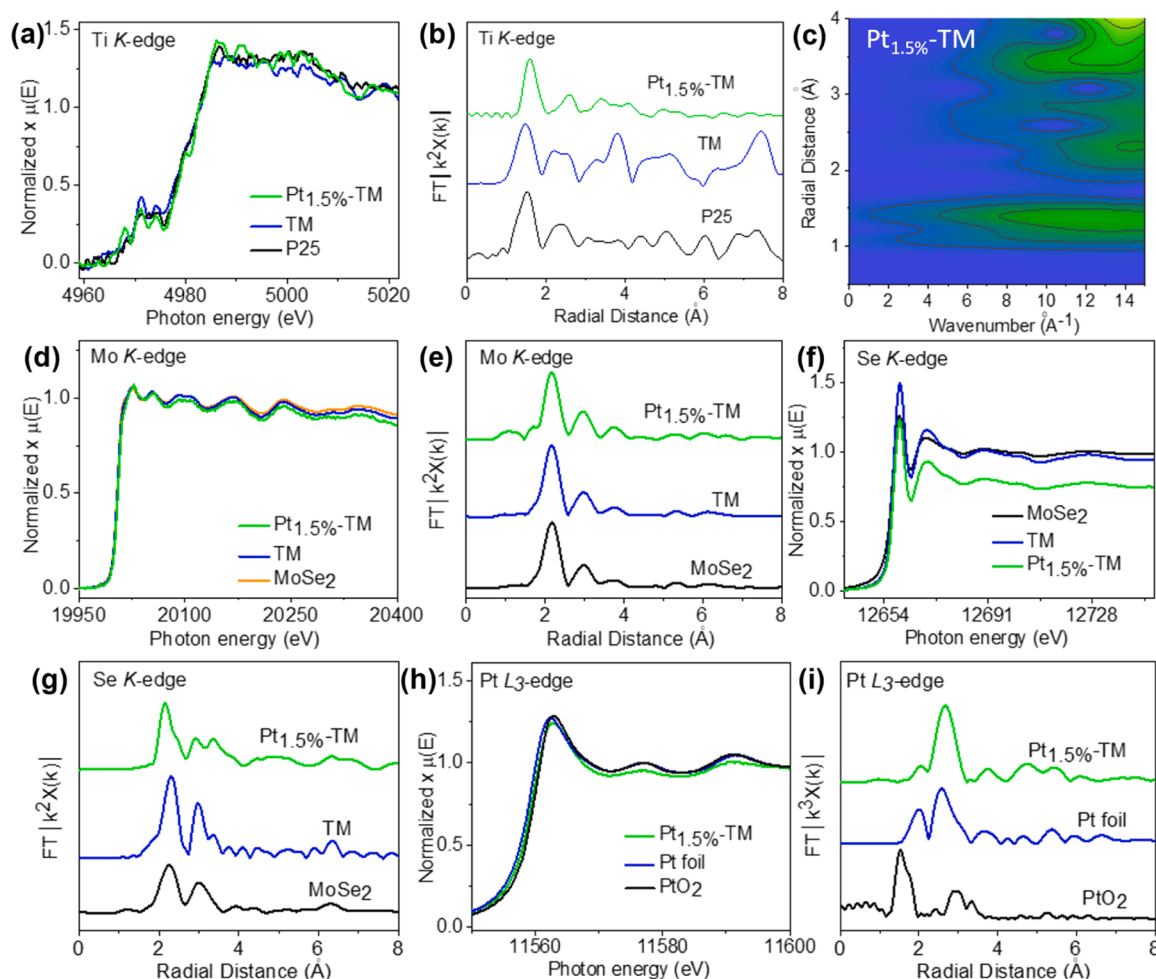


**Fig. 2.** (a) XRD patterns and (b-c) Raman spectra of P25, TM, and Pt<sub>1.5%</sub>-TM. High-resolution XPS spectra of Pt<sub>1.5%</sub>-TM: (d) C 1s, (e) Ti 2p, (f) O 1s, (g) Mo 3d, (h) Se 3d, and (i) Pt 4f.

529.76, 529.98, and 531.75 eV are assigned to Ti–O–Ti, Ti–O–Mo, and Ti–O–H, respectively (Fig. 2f)[30]. The Mo 3d spectrum confirms the successful retention of the metallic 1T phase despite the addition of the Pt co-catalyst (Fig. 2g)[31]. The dominant doublet at 227.96 eV and 231.09 eV is assigned to the 1T-MoSe<sub>2</sub> phase, while the lower intensity peaks at 228.62 eV and 232.43 eV corresponds to the residual 2H phase [32,33]. The presence of Mo<sup>6+</sup> species is also noted at 233.89 eV and 235.25 eV, alongside the Se 3s peak at 231.92 eV [26,34]. The oxidized Mo component becomes more pronounced in TM compared to the exfoliated sample. This can be attributed to the strong interfacial interaction between MoSe<sub>2</sub> and TiO<sub>2</sub>, which can induce partial charge redistribution at the interface to stabilize oxidized Mo species. The Se 3d spectrum mirrors this trend, showing a significant downshift consistent with the metallic 1T character (Fig. 2h)[31]. The Pt 4f spectrum provides evidence for the successful deposition of Pt NPs. The doublet observed at 70.35 and 73.64 eV confirms that Pt exists in its metallic (Pt<sup>0</sup>) state (Fig. 2i), which is ideal for facilitating charge transfer. The interfacial interaction between TiO<sub>2</sub> and MoSe<sub>2</sub>/Pt was confirmed by Ti 2p and O 1s XPS spectra (Fig. S9). The Ti 2p spectra showed a slight negative shift and peak broadening after MoSe<sub>2</sub> and Pt deposition, which can be attributed to interfacial charge redistribution and the partial formation of surface Ti<sup>3+</sup> species near the heterojunction, rather than bulk reduction of TiO<sub>2</sub>[11]. The O 1s binding energy shift indicates interfacial electronic coupling and charge redistribution at equilibrium, rather than the dynamic transport direction of photoexcited carriers.

This is consistent with Mott–Schottky results showing a built-in electric field and improved charge separation, as discussed in the mechanism section.

X-ray absorption spectroscopy (XAS) was conducted to observe the local electronic and geometrical structures around a selected element of TM and Pt<sub>1.5%</sub>-TM (Figs. 3 and S10–S14). Ti K-edge XANES (X-ray absorption near edge structure) and EXAFS (Extended X-ray absorption fine structure) provide insights into the interfacial modification of P25 (TiO<sub>2</sub>) upon formation of the TM and Pt<sub>1.5%</sub>-TM heterostructures. Ti K-edge XANES spectra show a slight shift of the absorption edge toward higher energy, along with subtle changes in the pre-edge features for TM and Pt<sub>1.5%</sub>-TM compared with pristine P25 (Fig. 3a). This shift indicates a decrease in electron density at Ti, suggesting electron transfer from TiO<sub>2</sub> to the MoSe<sub>2</sub> and Pt components. The modification of pre-edge features further reflects changes in Ti 3d–O 2p hybridization induced by interfacial interactions. Ti k-edge EXAFS analysis reveals a slight change in both the first-shell and higher-shell scattering features after MoSe<sub>2</sub> coupling and Pt deposition, indicating changes in the local coordination environment of Ti (Fig. 3b). The EXAFS fittings suggests that the Ti–O bond distance remains nearly unchanged, varying slightly from 1.96 Å for P25–1.95 Å for TM and 1.96 Å for Pt<sub>1.5%</sub>-TM (Fig. S10 and Table S2). In contrast, the coordination number decreases from 3.71 in P25–3.25 and 3.27 for TM and Pt<sub>1.5%</sub>-TM, respectively, accompanied by an increase in the Debye–Waller factor, suggesting a modest increase in local structural disorder upon MoSe<sub>2</sub> incorporation and Pt loading.



**Fig. 3.** X-ray absorption analysis (a, b) Ti K-edge XANES and Fourier-transformed EXAFS spectra of P25, TM, and Pt<sub>1.5%</sub>-TM, (c) wavelet transform (WT) analysis of Ti-K-edge of Pt<sub>1.5%</sub>-TM, (d, e) Mo K-edge XANES and Fourier-transformed EXAFS spectra of MoSe<sub>2</sub>, TM, and Pt<sub>1.5%</sub>-TM, (f, g) Se K-edge XANES and Fourier-transformed EXAFS spectra of MoSe<sub>2</sub>, TM, and Pt<sub>1.5%</sub>-TM, and (h, i) Pt L<sub>3</sub>-edge XANES and Fourier-transformed EXAFS spectra of Pt, PtO<sub>2</sub>, and Pt<sub>1.5%</sub>-TM.

These observations indicate that the TiO<sub>2</sub> lattice framework is largely preserved while the local Ti coordination environment is subtly modified through interfacial interactions. The corresponding  $k^3$ -weighted EXAFS spectra show discernible amplitude differences between P25, TM, and Pt<sub>1.5%</sub>-TM, further supporting changes in the local atomic environment surrounding Ti (Fig. S11). WT-EXAFS analysis exhibits dominant Ti–O coordination features without the appearance of high- $R$  contributions associated with Ti–Ti or Ti–Se coordination. This indicates the absence of new bulk Ti–Se or Ti–Pt phases and suggests that MoSe<sub>2</sub> and Pt interact with TiO<sub>2</sub> (Figs. 3c and S12).

Mo K-edge XANES spectra reveal that TM and Pt<sub>1.5%</sub>-TM exhibit nearly identical features to pure MoSe<sub>2</sub>, indicating that the electronic state of Mo remains largely unaffected by heterostructure formation (Fig. 3d). In the Mo K-edge FT-EXAFS spectra, two dominant peaks at  $\approx 2.14$  Å and  $2.94$  Å correspond to Mo–Se and Mo–Mo coordination, respectively, characteristic of MoSe<sub>2</sub> (Fig. 3e). For Pt<sub>1.5%</sub>-TM, a weak feature around  $\approx 1$  Å was observed, which can be attributed to slight Mo–O coordination, consistent with the oxidation signal also detected in XPS. Importantly, the overall spectral profiles of TM and Pt<sub>1.5%</sub>-TM closely resemble those reported for the 1T phase of MoSe<sub>2</sub>, suggesting that the layered MoSe<sub>2</sub> phase is preserved within the heterostructure. The  $k^3$ -weighted EXAFS oscillations further support this conclusion, as Mo atoms retain their local bonding configuration with only minor perturbations (Fig. S13a). Cao *et al.* reported the difference between the 1T and 2H phases for K-edge Mo, where the peaks of TM and Pt-TM closely resemble those of the 1T phase of MoSe<sub>2</sub> [35]. The Se K-edge

displays clear signatures of interfacial perturbation. The Se XANES near-edge intensity for TM and Pt<sub>1.5%</sub>-TM is decreased relative to pristine MoSe<sub>2</sub>, indicating changes in the Se unoccupied states consistent with interfacial electronic coupling or partial charge redistribution (Fig. 3f). The principal Se–Mo coordination peak appears at the same radial distance as in pristine MoSe<sub>2</sub>, indicating that the Se–Mo bond length is preserved (Fig. 3g). The  $k^3$ -weighted Se EXAFS oscillations show reduced oscillation amplitude (damping) for the heterostructure samples compared with pristine MoSe<sub>2</sub> (Fig. S13b).

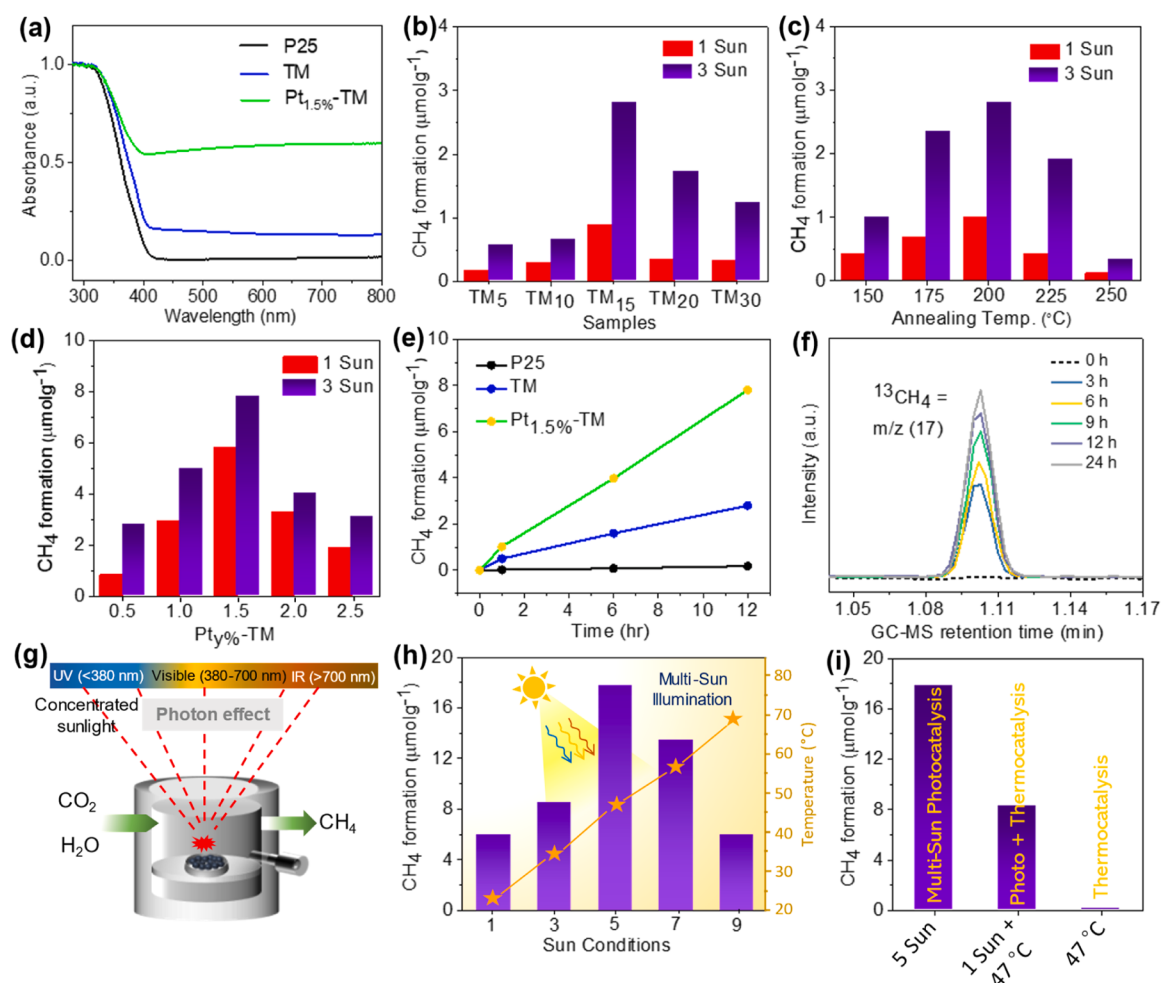
The Pt L<sub>3</sub>-edge XANES spectra show a white line intensity and edge position like the Pt foil, indicating a metallic Pt<sup>0</sup> state, consistent with XPS findings (Fig. 3h) [36]. Fourier-transformed EXAFS spectra reveal a prominent Pt–Pt peak at  $\sim 2.7$  Å, matching the foil and suggesting metallic NPs, with no significant Pt–O contribution (Fig. 3i). WT analysis of the Pt L<sub>3</sub>-edge EXAFS further supports the metallic nature of Pt in the catalyst (Fig. S14). The Pt foil exhibits a well-defined intensity maximum at  $R \approx 2.5$ – $2.8$  Å and  $k \approx 8$ – $10$  Å<sup>−1</sup>, characteristic of Pt–Pt coordination in metallic Pt. A similar feature is observed for Pt<sub>1.5%</sub>-TM, confirming the presence of metallic Pt NPs. However, compared to Pt foil, the WT feature in Pt<sub>1.5%</sub>-TM is noticeably broader and extends toward lower  $k$  values, which can be attributed to reduced coordination number, structural disorder, and size effects of Pt NPs on the TiO<sub>2</sub>–MoSe<sub>2</sub> support.

### 3.2. Optical properties and band structure analysis

In the ultraviolet-visible diffuse reflectance spectroscopy (UV-Vis-DRS), P25 exhibits an optical absorption edge at around 390 nm due to its broad bandgap. There was increased light absorption in the visible region of 400–800 nm for the TM (Figs. 4a and S15). While MoSe<sub>2</sub> loading on the surface of P25 does not significantly modify its inherent absorption edge [11]. Further improvement was observed after Pt deposition on TM, which can be attributed to the localized surface plasmon resonance (LSPR) [37]. Tauc's plot analysis was employed to evaluate the optical absorption characteristics and apparent bandgap evolution of P25, TM, and Pt<sub>1.5%</sub>-TM. For such multicomponent heterostructures, the derived bandgap values represent effective optical transitions of the composite system rather than intrinsic band edges of single phases. Tauc plot analysis reveals a narrowing of the optical bandgap from P25 (3.28 eV) to TM (3.14 eV) and further to Pt<sub>1.5%</sub>-TM (2.99 eV) (Fig. S16a). Beyond improved light harvesting, this electronic-structure modulation plays a critical role in governing CO<sub>2</sub>-reduction selectivity. The bandgap narrowing and formation of interfacial states facilitate more efficient charge excitation and accumulation, thereby increasing the steady-state electron density at the catalytic interface. This elevated electron population provides the necessary thermodynamic driving force and kinetic feasibility for the demanding multi-electron proton-coupled reduction of CO<sub>2</sub> beyond the

two-electron CO pathway toward deep hydrogenation to CH<sub>4</sub>. Consequently, the optimized electronic structure of Pt<sub>1.5%</sub>-TM favors CH<sub>4</sub> formation [38].

The valence band XPS (VB-XPS) was employed to determine the electronic band structures (Fig. S16b). It should be noted that VB-XPS measurements are performed under ultra-high vacuum conditions, whereas the photocatalytic reactions occur in the presence of H<sub>2</sub>O vapor. Surface hydration and adsorption of water molecules may slightly influence the band-edge positions of oxide photocatalysts [39]. Nevertheless, VB-XPS is widely used to estimate relative band alignment and provide qualitative insight into interfacial charge-transfer behaviour in photocatalytic systems. For the P25 standard, the valence band maximum (VBM) was determined to be 2.56 eV, which is consistent with the characteristic band edge for mixed-phase TiO<sub>2</sub>[40,41]. Given the optical band gap of 3.28 eV, the conduction band minimum (CBM) of P25 is positioned at −0.72 eV vs. NHE (Fig. S16c). The VB-XPS of TM shows a VBM at 2.30 eV; such a shift of the VBM towards the vacuum level is attributed to the electronic interface formed between P25 and MoSe<sub>2</sub>. Upon the deposition of Pt, a further upward shift in the VBM to 2.27 eV was observed for the Pt<sub>1.5%</sub>-TM ( $E_g = 2.99$  eV), placing its CBM at −0.72 eV. These band positions are highly suitable for the photoreduction of CO<sub>2</sub> into CH<sub>4</sub>, as the conduction bands remain significantly more negative than the respective redox potentials of −0.53 eV and −0.24 eV vs. NHE.



**Fig. 4.** (a) UV-Vis-DRS of P25, TM, and Pt<sub>1.5%</sub>-TM. Photocatalytic CO<sub>2</sub> reduction to CH<sub>4</sub> under 1- and 3-sun illumination: (b) TM with varying MoSe<sub>2</sub> contents, (c) TM annealed at different temperatures, (d) Pt<sub>y%</sub>-TM, (e) time-dependent CO<sub>2</sub> reduction performance of P25, TM, and Pt<sub>1.5%</sub>-TM, (f) GC-MS chromatogram confirming <sup>13</sup>CH<sub>4</sub> formation for Pt<sub>1.5%</sub>-TM, (g) solar spectral distribution used for multi-sun illumination, (h) photocatalytic performance of Pt<sub>1.5%</sub>-TM under different sun illuminations with corresponding reaction temperatures, and (i) comparison of CO<sub>2</sub> reduction under photocatalysis (1 and 5-Sun photocatalysis), photothermal (1-Sun + 47 °C) and thermocatalysis at an equivalent temperature (47 °C) corresponding to the 5-Sun condition (dark reaction).

### 3.3. Photocatalytic CO<sub>2</sub> reduction

The photocatalytic CO<sub>2</sub> reduction experiments were conducted in the gas phase of CO<sub>2</sub> (1000 ppm) and H<sub>2</sub>O vapor. Given that the atmospheric CO<sub>2</sub> level is currently ~420–470 ppm, developing catalysts capable of operating efficiently under CO<sub>2</sub>-scarce environments is critically important. The photocatalytic system is presented in Fig. S17 and Table S3, and the results are shown in Figs. 4b–i and S18. All the samples were tested under 1-sun and 3-sun illumination to study the photonic effect on catalysis. Pure P25 showed very low activity for CO<sub>2</sub> reduction. However, introducing varying amounts of MoSe<sub>2</sub> (Fig. 4b, c), followed by the deposition of Pt NPs (Fig. 4d), significantly increased CO<sub>2</sub> reduction activity. In the TM, the production of CH<sub>4</sub> increased with higher MoSe<sub>2</sub> concentration, reaching an optimal yield of 0.90  $\mu\text{mol g}^{-1}$  under 1-sun light. Under 3-sun light, the photocatalytic activity was more than three times greater, achieving 2.8  $\mu\text{mol g}^{-1}$  compared to 1-sun conditions. The annealing temperature during TM preparation was optimized by evaluating catalysts treated at 150–250 °C. The catalyst prepared at 200 °C has the highest activity, which is attributed to improved interfacial contact between TiO<sub>2</sub> and MoSe<sub>2</sub> that facilitates charge transfer. A decrease in activity at higher temperatures was observed, possibly due to partial restacking or structural modification of MoSe<sub>2</sub> nanosheets, which reduces accessible active sites. The Pt-deposited catalysts further enhanced CO<sub>2</sub> reduction activity, where CH<sub>4</sub> was observed as a major product, while trace of C<sub>2</sub>H<sub>6</sub> formation. (Fig. 4d and S18). The optimal Pt<sub>1.5%</sub>-TM produced 5.84  $\mu\text{mol g}^{-1}$  under 1-sun and 7.81  $\mu\text{mol g}^{-1}$  under 3-sun illumination. Increasing the amount of Pt beyond 1.5 wt% led to a decrease in CO<sub>2</sub> reduction activity, suggesting that excess Pt may form clusters that act as recombination centers, hindering performance. Compared to the TM, the Pt<sub>1.5%</sub>-TM showed 6.4 times higher activity under 1-sun and 2.7 times higher under 3-sun light. Although CH<sub>4</sub> was identified as the dominant carbonaceous product, trace amounts of C<sub>2</sub>H<sub>6</sub> were also detected under light irradiation conditions for the Pt<sub>y%</sub>-TM samples (Figure S18a). Nevertheless, the selectivity toward CH<sub>4</sub> remained  $\approx$  98%. Because the reaction takes place at the gas-solid interface in the absence of a bulk liquid medium, the formation of soluble liquid-phase byproducts (e.g., CH<sub>3</sub>OH and HCOOH) is bypassed.

The time-dependent formation of CH<sub>4</sub> during CO<sub>2</sub> reduction was analyzed for P25, TM, and Pt<sub>1.5%</sub>-TM, where a significant increase in the CH<sub>4</sub> formation rate was observed for the TM and Pt<sub>1.5%</sub>-TM. Further, no notable change was observed in P25 over time (Fig. 4e). Fig. S18b provides a comparison of photocatalytic activity between P25, TM, and Pt<sub>1.5%</sub>-TM, along with several control experiments. No CH<sub>4</sub> was detected in the dark or when CO<sub>2</sub> was absent (only He present), and tests without photocatalysts confirmed that the reaction depended on both light and CO<sub>2</sub>. The gas chromatography results matched standard CH<sub>4</sub> references (Fig. S19a), confirming that CH<sub>4</sub> was produced through photocatalytic reduction of CO<sub>2</sub>. To validate the carbon source for CH<sub>4</sub> production during photocatalysis, isotopic labeling was conducted (Fig. 4f). The formation of CH<sub>4</sub> at  $m/z = 17$  was clearly detected over time, confirming the gradual generation of <sup>13</sup>CH<sub>4</sub> during the reaction under light irradiation.

The CH<sub>4</sub> selectivity ( $\approx$ 98%) arises from the synergistic integration of catalyst composition and electronic structure. The Pt and MoSe<sub>2</sub> cocatalysts provide active sites for CO<sub>2</sub> adsorption and activation, stabilizing key reaction intermediates such as \*CO and \*CHO, as evidenced by in-situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) and density functional theory (DFT) simulations. This suppresses the premature desorption of CO and promotes deep hydrogenation pathways. Pt NPs act as efficient hydrogenation cocatalysts, accelerating proton-coupled electron transfer processes and facilitating the stepwise conversion of \*CO into CH<sub>4</sub>. The charge transfer enabled by the TiO<sub>2</sub>-MoSe<sub>2</sub>-Pt tri-junction ensures accumulation of photogenerated electrons at the reaction interface. Under concentrated irradiation, the mild increase in temperature enhances surface reaction

kinetics and CH<sub>4</sub> desorption, overcoming the activity-selectivity trade-off. Furthermore, no CO was detected in the gaseous products (Fig. S19b), although \*CO is identified as a key reaction intermediate by in situ DRIFTS. This suggests that surface-bound \*CO is rapidly hydrogenated to \*CHO and subsequent intermediates, preventing its accumulation and desorption. No C<sub>2</sub>H<sub>4</sub> was detected during the CO<sub>2</sub> reduction tests (Fig. S19c). A trace of C<sub>2</sub>H<sub>6</sub> was detected in the gas chromatograph (Fig. S19d). Despite the presence of H<sub>2</sub>O vapor as the proton source, no H<sub>2</sub> evolution was detected (Fig. S19e). This behavior demonstrates that photogenerated electrons and surface H<sup>+</sup> drive CO<sub>2</sub> hydrogenation by rapidly converting carbon intermediates, rather than reducing protons. The hydrogenation ability of 1T-MoSe<sub>2</sub>/Pt, together with enhanced \*CO adsorption, suppresses H<sub>2</sub> evolution and CO formation, leading to high CH<sub>4</sub> selectivity. To elucidate the underlying mechanism governing this behavior, we carried out DFT calculations, and the characteristics of the \*CO and other intermediates were analyzed via in situ FTIR spectroscopy under light irradiation.

The catalyst shows good stability over four cycles, maintaining CH<sub>4</sub> production, but its activity decreases in the fifth cycle (Fig. S18c). The catalyst largely maintains its crystal structure and chemical state after CO<sub>2</sub> reduction tests (Fig. S20). No significant changes in XRD and Raman were observed before and after the CO<sub>2</sub> reduction. XPS spectra of Ti 2p and O 1s show no changes in chemical states after reaction (Fig. S21), while the intensities of Mo, Se, and Pt slightly decreased. To further understand the structural evolution during photocatalysis, XAFS analysis was performed on the Pt<sub>1.5%</sub>-TM catalyst before and after CO<sub>2</sub> photoreduction. After reaction, a slight decrease in the Ti–O bond length (from 1.96 to 1.94 Å) and a moderate increase in coordination number (from 3.27 to 3.74) were observed, indicating mild local surface reconstruction (Table S2). To scrutinize morphological features, post-reaction TEM/HR-TEM imaging was performed after the fifth cycle (Fig. S22). The images reveal that the overall structural framework of the ternary hybrid is sustained, and the Pt nanoparticles remain anchored and dispersed across the matrix without undergoing severe agglomeration. Consequently, the decline in CH<sub>4</sub> evolution during the fifth cycle is attributed to the combined effects of these minor cocatalyst surface evolutions and accumulated local structural reconstructions during long-term operational testing.

Light intensity plays a crucial role in CO<sub>2</sub> reduction by influencing charge-carrier generation and surface reaction kinetics [42]. We examined the impact of multi-sun illumination on the CH<sub>4</sub> formation efficiency of Pt<sub>1.5%</sub>-TM (Fig. 4g). Under 1-sun illumination, CH<sub>4</sub> production was limited due to relatively low photon flux. Increasing the light intensity significantly enhanced CH<sub>4</sub> production, reaching a maximum of 17.81  $\mu\text{mol g}^{-1}$  at 5-sun illumination. This enhancement is primarily attributed to the increased availability of photons, which promotes higher rates of charge carrier generation and improves photocatalytic activity. A decline in CH<sub>4</sub> production beyond 5-sun illumination is observed, which may be attributed to increased charge carrier recombination at higher irradiation intensities [44,45]. During multi-sun illumination, a moderate increase in reactor temperature was observed (e.g.,  $\sim$ 47 °C at 5 suns, Fig. 4h). To decouple the respective contributions of the photonic effect and potential photothermal synergistic acceleration, two control experiments were performed (Fig. 4i). First, a pure thermocatalytic dark reaction at 47 °C yielded negligible CH<sub>4</sub>. Second, a control experiment combining 1-Sun illumination with external heating to 47 °C (1-Sun + 47 °C) was conducted. Only a slight increase in CH<sub>4</sub> evolution was observed compared to the ambient 1-sun test. This minor enhancement indicates that while the elevated temperature provides a slight kinetic acceleration to the photogenerated carriers, it cannot account for the drastic performance surge witnessed under multi-sun conditions. Therefore, although localized heating effects under concentrated illumination cannot be completely excluded, the prominent enhancement under 5-sun illumination is unequivocally dominated by the increased photon flux, which drastically boosts charge carrier generation rates [43]. To contextualize the solar-driven activity

of the Pt<sub>1.5%</sub>-TM photocatalyst, a comprehensive quantitative comparison with recently reported state-of-the-art benchmarks evaluated under simulated concentrated sunlight is summarized in Table S4.

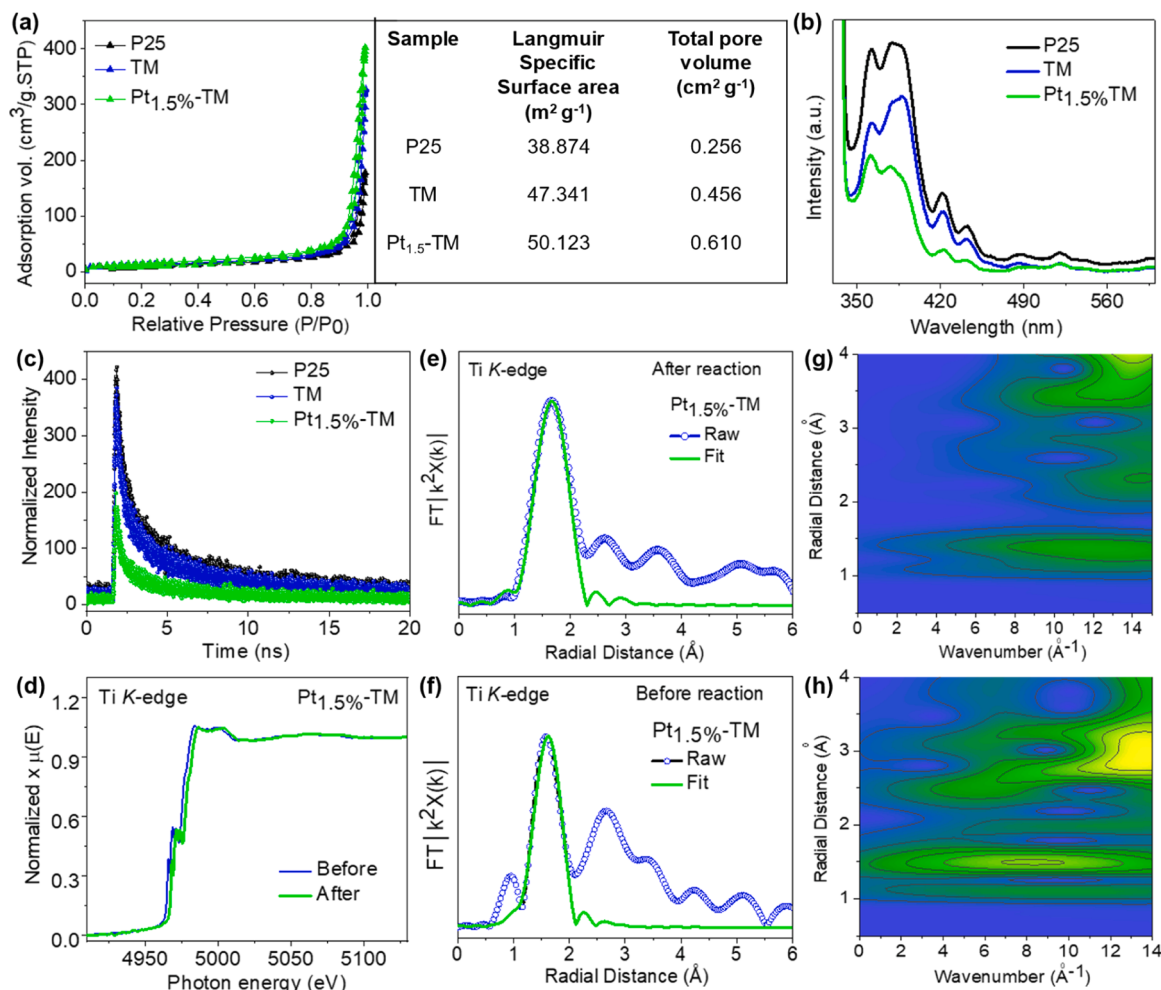
### 3.4. Surface properties and charge transfer study

The N<sub>2</sub> adsorption/desorption characteristics of P25, TM, and Pt<sub>1.5%</sub>-TM were used to establish their specific surface areas and pore size distributions. All the catalysts show a type IV isotherm, indicating typical mesoporous characteristics (Figs. 5a and S23). The Langmuir-specific surface area and the total pore volume for the catalysts are shown in the insets of Fig. 5a. The BET surface area of P25 was 38.874 m<sup>2</sup> g<sup>-1</sup>. TM showed a larger micropore surface area (47.341 m<sup>2</sup> g<sup>-1</sup>) than P25, further increasing in Pt<sub>1.5%</sub>-TM (50.123 m<sup>2</sup> g<sup>-1</sup>). The average pore size for P25, TM, and Pt<sub>1.5%</sub>-TM was 0.256, 0.456, and 0.610 cm<sup>3</sup> g<sup>-1</sup>, respectively. These findings suggest that Pt<sub>1.5%</sub>-TM could offer a greater surface area and more active sites, thereby enhancing CO<sub>2</sub> adsorption and increasing photocatalytic activity [46,47].

Charge transfer in the catalyst was studied by photoluminescence (PL) spectroscopy (Figs. 5b and S24). PL quenching from P25 → TM → Pt<sub>1.5%</sub>-TM indicates enhanced charge separation and electron transfer after MoSe<sub>2</sub> and Pt deposition. Time-resolved PL (TRPL) analysis shows average decay lifetimes of 2.45, 2.31, and 1.71 ns for P25, TM, and Pt<sub>1.5%</sub>-TM, respectively (Fig. 5c and Table S5). The Pt<sub>1.5%</sub>-TM exhibits the lowest decay time, indicating fast charge transfer. This improved mobility reflects more free electrons in Pt<sub>1.5%</sub>-TM and suppressed

electron-hole recombination via interfacial charge transfer [48]. This pronounced acceleration of the non-radiative decay rate serves as kinetic evidence that photogenerated electrons are rapidly swept across the cascading interfaces, successfully intercepting bulk radiative recombination. The electrochemical analyses (cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS)) were performed for P25, TM, and Pt<sub>1.5%</sub>-TM (Fig. S25). All catalysts exhibited typical redox loops (Fig. S25a). Pt<sub>1.5%</sub>-TM showed the largest redox peak separation, indicating superior electronic and catalytic properties [26]. EIS revealed that P25 had the highest charge-transfer resistance, while TM and Pt<sub>1.5%</sub>-TM showed lower resistance due to improved interfacial conductivity between MoSe<sub>2</sub>, Pt, and P25 (Fig. S25b). The enhanced conductivity of TM arises from the 1T-metallic nature of MoSe<sub>2</sub> [49].

Charge transfer and structural evolution in Pt<sub>1.5%</sub>-TM were further analyzed using Ti K-edge XANES, FT-EXAFS (Fig. 5d-f and Table S2), and wavelet transforms (Fig. 5g, h) before and after CO<sub>2</sub> reduction. The post-reaction XANES spectrum shows a slight edge shift toward higher energy. This suggests a minor decrease in electron density around Ti, consistent with electron redistribution during photocatalysis. FT-EXAFS analysis reveals a marginal change in the Ti–O bond distance (1.96 → 1.94 Å) and an increase in coordination number (3.27 → 3.74), which indicates a modest reduction in local disorder and partial structural stabilization after reaction. WT analysis shows slightly more localized intensity features after reaction, indicating a more uniform Ti–O coordination environment and reduced local disorder, consistent with the EXAFS fitting results. These results suggest that the TiO<sub>2</sub> framework



**Fig. 5.** (a) BET surface area, (b, c) PL and TRPL of P25, TM, and Pt<sub>1.5%</sub>-TM, (d) Ti K-edge XANES, (e, f) Ti K-edge FT-EXAFS fits (before and after), and (g, h) wavelet transforms of k<sup>3</sup>-weighted EXAFS signals before and after CO<sub>2</sub> reduction of Pt<sub>1.5%</sub>-TM.

remains structurally stable, with some local coordination and surface changes occurring during the photocatalytic process. DFT calculations on the MoSe<sub>2</sub>-TiO<sub>2</sub> heterojunction and a Pt<sub>13</sub> cluster on MoSe<sub>2</sub> also confirmed charge transfer, and the flow of electrons is TiO<sub>2</sub> → MoSe<sub>2</sub> → Pt<sub>13</sub> (discussed in detail in the section on DFT simulations of charge transfer).

Surface reactions, such as reactant adsorption/desorption on the catalyst surface, have critical steps in photocatalysis; therefore, CO<sub>2</sub>-temperature-programmed desorption (TPD) analysis was utilized to investigate the interaction of CO<sub>2</sub> reactant on the surface of P25, TM, and Pt<sub>1.5%</sub>-TM (Fig. S26). All three catalysts showed different CO<sub>2</sub>-TPD patterns depending on the adsorption ability of the catalyst, i.e., weak, moderate, and strong adsorption [50]. P25 showed a broad peak between ~80–410 °C centered at ~380 °C, ascribed to the strong adsorption of CO<sub>2</sub>. In the case of the TM, a comparatively sharp peak (~80–250 °C) centered at approximately 200 °C can be observed, which may be due to CO<sub>2</sub> adsorption via a combination of weak and moderate chemical bonds. The sharp peak and shift towards a lower temperature in TM than P25 indicate that MoSe<sub>2</sub> plays a dominant role in CO<sub>2</sub> adsorption. However, the peak was further shifted towards a higher temperature in the Pt<sub>1.5%</sub>-TM, appearing above 250 °C, ascribed to the desorption of moderately adsorbed CO<sub>2</sub> molecules. Thermodynamically, the catalyst with moderately adsorbed CO<sub>2</sub> provides more active sites for the adsorption/activation of CO<sub>2</sub> molecules [50,51]. Consequently, adsorption of CO<sub>2</sub> molecules takes place through multiple C of CO<sub>2</sub> to the catalysts (probably Se and Pt), so that the activation is more dominant in Pt<sub>1.5%</sub>-TM. Although CO<sub>2</sub>-TPD is conducted under dark conditions, it reflects the intrinsic adsorption properties of the catalyst. Under illumination, adsorption behavior may vary. However, moderately bound CO<sub>2</sub> species are expected to facilitate efficient adsorption-activation-desorption during photocatalysis.

Photocatalytic CO<sub>2</sub> reduction requires multielectron transfer, as single-electron pathways are energetically unfavorable (−1.9 eV vs. NHE) [52]. A noticeable decrease in VB values for Pt<sub>1.5%</sub>-TM compared to P25 and TM indicates charge transfer from the P25 lattice to the MoSe<sub>2</sub> and Pt cocatalysts. This shift is corroborated by Raman spectra, where a considerable shift in the E<sub>g</sub> signal at around 150 cm<sup>−1</sup> is observed following Pt deposition. A correlation between VB shifts and Raman active modes has been previously reported in the literature [22]. To clarify the directionality of charge migration, Mott-Schottky analysis was performed (Fig. S27). The flat-band potential of −0.60 V and −0.43 V (vs. Ag/AgCl) for P25 and MoSe<sub>2</sub>, respectively, reveals that the CBM of TiO<sub>2</sub> is positioned at a more negative potential than that of MoSe<sub>2</sub>. This configuration yields an intrinsic 170 mV potential gradient that naturally drives the directional migration of photogenerated electrons from the more negative CB of TiO<sub>2</sub> to the lower-lying CB of MoSe<sub>2</sub>. This spatial routing is strongly supported by DFT Bader charge analysis, which indicates that an additional photoelectron preferentially localizes on the MoSe<sub>2</sub> domain (67.5%) compared to TiO<sub>2</sub> (32.5%), confirming a highly directed interfacial electron flux under illumination. XPS analysis of the O 1 s core level reveals a negative binding energy shift at equilibrium (dark conditions), suggesting a minor static electron accumulation on the TiO<sub>2</sub> surface. This implies the coexistence of static interfacial charge redistribution at the heterojunction to equilibrate Fermi levels and dynamic photoinduced electron transfer during catalysis. The integration of MoSe<sub>2</sub> and Pt NPs further narrows the effective bandgap and optimizes the energy band alignment. The high-conductivity 1T-lattice functions as an efficient electronic bridge, funneling the electrons downhill from TiO<sub>2</sub> to the Pt active sites. This synergistic effect overcomes the thermodynamic barriers to CO<sub>2</sub> reduction, leading to the improved photocatalytic efficiency observed in Pt<sub>1.5%</sub>-TM [38]. Furthermore, coumarin photoluminescence testing (Fig. S28) demonstrates a substantial boost in \*OH radical formation over the Pt<sub>1.5%</sub>-TM catalyst compared to its binary and pristine counterparts. This elevated oxidation-side activity confirms that photo-generated holes are successfully localized and utilized on the TiO<sub>2</sub>

surface, achieving a highly desirable spatial decoupling of the redox sites.

### 3.5. In-situ DRIFT for CO<sub>2</sub> reduction mechanisms

Under solar irradiation, Pt<sub>1.5%</sub>-TM generates electron-hole pairs as electrons are excited from the VB to the CB of TiO<sub>2</sub>. Electrons transfer to MoSe<sub>2</sub> (and Pt NPs in Pt<sub>1.5%</sub>-TM) to reduce adsorbed CO<sub>2</sub>, while holes in TiO<sub>2</sub> oxidize H<sub>2</sub>O. This distribution of charge facilitates efficient CO<sub>2</sub> reduction and water oxidation. To confirm the oxidation half-reaction, O<sub>2</sub> evolution during photocatalytic CO<sub>2</sub> reduction over Pt<sub>1.5%</sub>-TM was measured. The O<sub>2</sub> generation was observed (Fig. S19f), demonstrating that water oxidation serves as a proton source for CH<sub>4</sub> formation, thereby establishing a closed photocatalytic redox cycle [53].

In situ FTIR spectra were recorded using a DRIFTS accessory equipped with a controlled reaction chamber (Fig. S29). The catalyst was pretreated under flowing gas and subsequently exposed to the CO<sub>2</sub>/H<sub>2</sub>O reaction environment. Spectra were collected under dark conditions followed by light illumination at different irradiation times to monitor the evolution of surface intermediates during the photocatalytic CO<sub>2</sub> reduction process. The results are compared with dark and light illumination (Fig. 6a–d). The spectrum at 0 min corresponds to the background after three cycles of CO<sub>2</sub> + H<sub>2</sub>O purging and chamber saturation before light irradiation. Therefore, adsorption peaks of CO<sub>2</sub> and H<sub>2</sub>O are present. The peaks related to the CO<sub>2</sub> adsorption through monodentate (m-CO<sub>3</sub><sup>2−</sup> at 1326.08 cm<sup>−1</sup>) or bidentate carbonate (b-CO<sub>3</sub><sup>2−</sup> at 1383 & 1580 cm<sup>−1</sup>) and -OH stretching (H<sub>2</sub>O at 1649.90 cm<sup>−1</sup>) can be seen in the dark condition [54,55]. The reaction intermediate peaks emerge progressively only after light irradiation. For example, the intensity of the m-CO<sub>3</sub><sup>2−</sup> peak (1326.08 cm<sup>−1</sup>) and b-CO<sub>3</sub><sup>2−</sup> (1386.53 cm<sup>−1</sup>) slightly decreased as the reaction proceeded, suggesting the consumption of surface carbonate species during the reaction. The peaks at 1718.2 cm<sup>−1</sup> (C=O stretch), ~2080 cm<sup>−1</sup> (CO stretch), and 2821.14, 2896.66, and 2944.81 cm<sup>−1</sup> (C-H stretch) begin to appear after ~10 min of illumination and become more pronounced with increasing irradiation time (Fig. 6c, d) [56,57]. The peak at 1718.2 cm<sup>−1</sup> corresponds to the carboxyl (\*COOH) intermediate (surface-bound \*COOH) [58], accompanied by C-H stretches at 2896.66 and 2944.81 cm<sup>−1</sup>, consistent with its formation via COO<sup>−</sup> protonation early in the reduction pathway. The C-H stretch at 2821.14 cm<sup>−1</sup> suggests contributions from the \*CHO intermediate (e.g., formaldehyde), as its C-H stretch (~2700–2800 cm<sup>−1</sup>) is lower than typical aliphatic C-H modes. The higher C-H stretches (2896.66, 2944.81 cm<sup>−1</sup>) also support \*CH<sub>2</sub> and \*CH<sub>3</sub> intermediates formed later via hydrogenation. The absence of CO in gas chromatography tests (Fig. S19b) indicates rapid conversion of \*CO to downstream intermediates (\*CHO, \*CH<sub>2</sub>, \*CH<sub>3</sub>), driving CH<sub>4</sub> formation. The competitive branching between CO escape and deeper reduction is fundamentally dictated by the binding energy of the intermediate; highly active metal-cocatalyst and semiconductor configurations excel at maintaining a robust binding affinity for photogenerated \*CO species, raising the thermodynamic barrier for desorption to drive high CH<sub>4</sub> selectivity [59–61].

### 3.6. DFT simulations for the band alignment, charge transfer, and reaction mechanism

To understand the theoretical band positions in the Pt-TM interface, hybrid DFT calculations (using the HSE06 functional) were performed for all individual components, TiO<sub>2</sub>, MoSe<sub>2</sub>, Pt, and the most stable TiO<sub>2</sub> (101, anatase)-2H-MoSe<sub>2</sub>(001) interface (Fig. S30). We computed densities of states for four systems (to ascertain absolute band positions): TiO<sub>2</sub> (anatase bulk), TiO<sub>2</sub> (101, anatase), MoSe<sub>2</sub> (2H, 001), and TiO<sub>2</sub> (101, anatase)-MoSe<sub>2</sub> (2H, 001) interface (Fig. S31). The local potential for these four systems, and for Pt-(111) and 1T-MoSe<sub>2</sub>(001) surfaces, is provided in Fig. S32. A vacuum-aligned band energy diagram (Fig. S33) was constructed to clarify the relative band positions of TiO<sub>2</sub>, MoSe<sub>2</sub>,

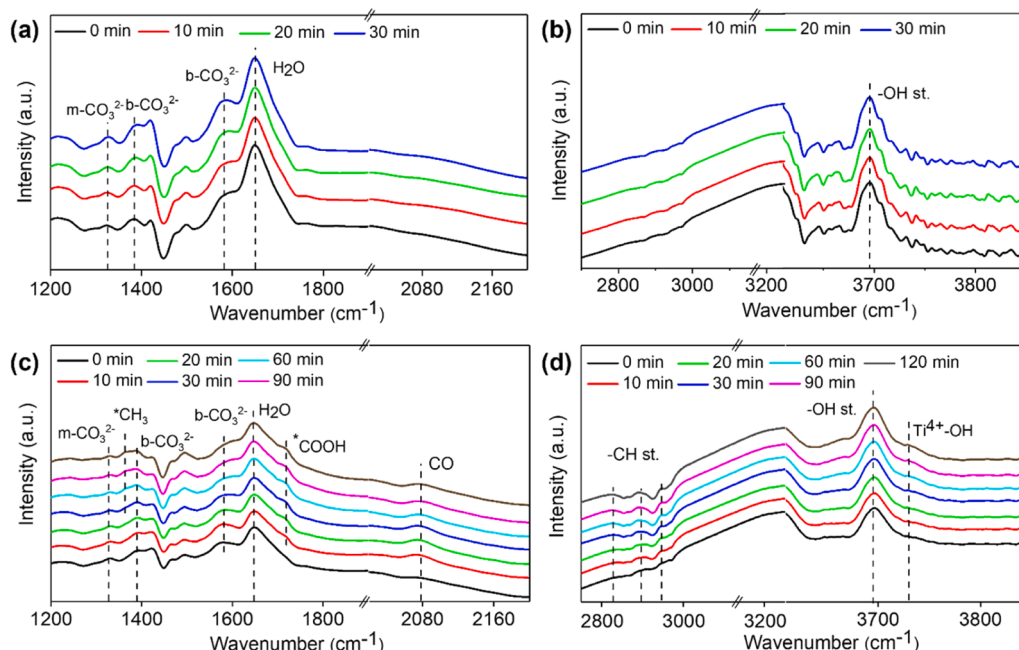


Fig. 6. In situ DRIFT spectra of Pt<sub>1.5%</sub>-TM under (a, b) dark and (c, d) light illumination at different time intervals.

and Pt and their implications for interfacial charge transfer. For anatase TiO<sub>2</sub> (101), CBM and VBM (with respect to  $E_{vac} = 0$ ) are located at  $-4.44$  eV and  $-7.67$  eV, respectively, corresponding to a band gap of  $3.23$  eV. 1T-MoSe<sub>2</sub> exhibits a work function of  $4.63$  eV, while Pt (111) shows a deeper work function of  $5.76$  eV. For completeness, the 2H-MoSe<sub>2</sub> reference phase has CBM and VBM at  $-3.92$  eV and  $-5.54$  eV, respectively ( $E_g = 1.62$  eV). TiO<sub>2</sub> has the deepest valence band, consistent with its role as the hole-accumulating oxidation site, whereas the Pt Fermi level lies significantly below the TiO<sub>2</sub> CBM, providing a strong thermodynamic driving force ( $\approx 1.3$  eV) for downhill electron transfer from photoexcited TiO<sub>2</sub>. Despite a higher CBM of MoSe<sub>2</sub> (2H), compared to CBM<sub>TiO2</sub>, the PDOS in Fig. S31 suggests a significant narrowing of the gap upon interfacial contact.

The Bader charge analysis on the optimized structure of this TiO<sub>2</sub>-MoSe<sub>2</sub> heterojunction shows the natural flow of electrons from MoSe<sub>2</sub> → TiO<sub>2</sub> under dark conditions, by a transfer of  $0.206 e^-$ . However, delta-SCF calculations with one additional electron in the system (an approximation to mimic photoelectron localization on this heterojunction) showed that MoSe<sub>2</sub> localizes two-thirds of this additional electron (Fig. 7a), which suggests that the direction of flow of electrons indeed reverses under illuminated conditions (TiO<sub>2</sub> → MoSe<sub>2</sub>).

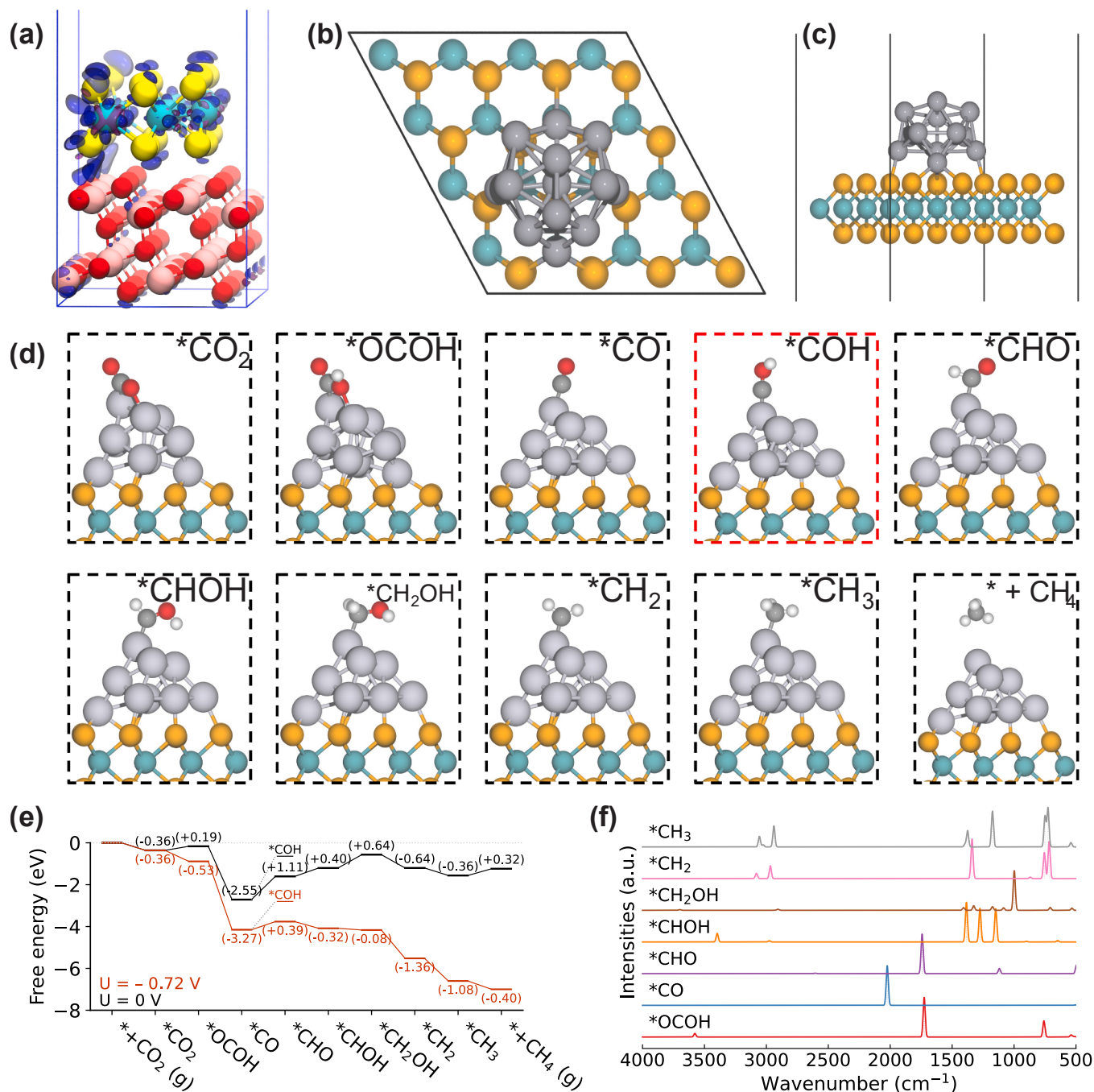
A Pt<sub>13</sub> NP interfaced on the MoSe<sub>2</sub> 001 structure was constructed as a cocatalyst model to examine the CO<sub>2</sub>RR mechanism (Fig. 7b, c). Bader charge analysis of the Pt<sub>13</sub>-MoSe<sub>2</sub> cocatalyst model showed that the Pt<sub>13</sub> cluster receives  $0.556 e^-$  charge from MoSe<sub>2</sub> (Fig. S34). The reaction mechanism is further derived from the examination of a single CO<sub>2</sub> molecule on the Pt<sub>13</sub>-MoSe<sub>2</sub> interface, followed by the determination of all the possible intermediates during the several PCET reactions (Fig. 7d, top view provided in Fig. S35). The  $^{*}CO_2$  intermediate forms with a binding energy of  $-0.36$  eV, with a Pt-C ( $1.98 \text{ \AA}$ ), Pt-O ( $2.04 \text{ \AA}$ ), and with an O-C-O angle of  $129^\circ$ . This step is followed by a slightly uphill ( $+0.19$  eV) PCET to form  $^{*}COOH$ . Under the assumption that the CBM for Pt<sub>1.5%</sub>-TM =  $-0.72$  eV, the corrected relative energy for  $^{*}CO_2 \rightarrow ^{*}COOH$  would be  $-0.53$  eV. The further reaction energy profile shown in Fig. 7e thus has both  $U = 0$  and CBM<sub>Pt1.5-TM</sub> corrected reference and relative values of energy. A subsequent PCET forms stable  $^{*}COOH \rightarrow ^{*}CO$  absorbed on Pt with Pt-C ( $1.82 \text{ \AA}$ ) at  $-3.27$  eV. The reaction further progresses via  $^{*}CO \rightarrow ^{*}CHO \rightarrow ^{*}CHOH \rightarrow ^{*}CH_2OH \rightarrow ^{*}CH_2OH \rightarrow ^{*}CH_2 \rightarrow ^{*}CH_3 \rightarrow ^{*}CH_4$  with  $^{*}CO \rightarrow ^{*}CHO$  being the most uphill step

with  $+0.39$  eV (CBM<sub>Pt-TM</sub> corrected, at  $U = 0, +1.11$  eV). From  $^{*}CH_2$ , the reaction is downhill to form  $^{*}CH_3$  with  $-1.08$  eV and finally desorbs CH<sub>4</sub> via successive PCET. Other reactions, e.g.,  $^{*}CO \rightarrow ^{*}COH$  and  $^{*}CH_2OH \rightarrow CH_3OH$ , were at least  $2.0$  eV uphill at  $U = 0$  and thus were not analyzed further.

From the optimized geometries of all main intermediates, theoretical IR spectra were derived by computing vibration frequencies and Born effective charges with density functional perturbation theory. The simulated spectra predict vibrational peaks at  $1725 \text{ cm}^{-1}$  (compared to  $1718.2$  experimental) and  $2024 \text{ cm}^{-1}$  (compared to  $2080$  experimental), attributed to  $^{*}COOH$  and  $^{*}CO$ , respectively [62] (Fig. 7f), with small discrepancies likely due to surface adsorption effects. Additionally, DFT predicts a C=O stretch at  $1742 \text{ cm}^{-1}$  for the  $^{*}CHO$  intermediate, which aligns with the experimental peak at  $1718.2 \text{ cm}^{-1}$  and support its role after CO reduction. The theoretical pathway ( $^{*}CO \rightarrow ^{*}CHO \rightarrow ^{*}CHOH \rightarrow ^{*}CH_2OH$ ) with subsequent relative energies of  $+0.39$ ,  $-0.32$ , and  $-0.08$  eV (at  $U = -0.72$  V) indicates low energy barriers for these steps, facilitating progression to CH<sub>4</sub> via subsequent hydrogenation ( $^{*}CH_2OH \rightarrow ^{*}CH_2 \rightarrow ^{*}CH_3$ ). For intermediates,  $^{*}CHOH$ ,  $^{*}CH_2OH$ ,  $^{*}CH_2$ , and  $^{*}CH_3$ , characteristic -CH stretching is seen between  $2918$  and  $3038 \text{ cm}^{-1}$ , comparable to in situ DRIFT values ( $2821.14$ ,  $2896.66$ , and  $2944.81 \text{ cm}^{-1}$ ). Together, the integration of experimental observations, in situ DRIFTS, and DFT calculations provides a coherent and complementary picture of the multi-step CO<sub>2</sub> reduction pathway, linking intermediates to their energetic and vibrational characteristics and confirming the mechanistic rationale behind CH<sub>4</sub> formation.

#### 4. Conclusions

We provide a TiO<sub>2</sub>-based photocatalytic system with dual cocatalyst engineering that allows for highly selective CO<sub>2</sub>-to-CH<sub>4</sub> conversion under multisun irradiation. A directional charge-transfer channel (TiO<sub>2</sub> → MoSe<sub>2</sub> → Pt) that efficiently encourages electron migration and inhibits charge recombination is created by combining MoSe<sub>2</sub> and Pt as cooperative cocatalysts. Direct experimental evidence for interfacial charge redistribution and the creation of internal electric fields is provided by comprehensive spectroscopic and electrochemical investigations, including XPS, XANES/EXAFS, Mott-Schottky, and TRPL. By showing preferential electron buildup at Pt sites and stabilization of



**Fig. 7.** (a) Electronic charge localization in TiO<sub>2</sub>(101)-MoSe<sub>2</sub>(001) heterostructure computed from the  $\Delta\text{SCF}$  approximation to a photoelectron generation, (b) top and (c) side view of Pt<sub>13</sub>-MoSe<sub>2</sub> interface, (d) side view of optimized geometries for CO<sub>2</sub> to CH<sub>4</sub> conversion on Pt-MoSe<sub>2</sub> surface from DFT (top view is provided as Fig. S35), (e) mechanistic pathway for CO<sub>2</sub> to CH<sub>4</sub> conversion, at 0 V, and also corrected for CBM for Pt<sub>1.5</sub>%-TM = -0.72 eV, and (f) simulated vibrational spectra for main path intermediate structures shown in (d) from density functional perturbation theory.

important chemical intermediates ( $^*\text{CO}$  and  $^*\text{CHO}$ ), which are essential for CH<sub>4</sub> selectivity, our DFT calculations support the experimental results. This combined experimental-theoretical approach establishes a consistent reaction pathway. Furthermore, quantitative compositional analysis, isotope labeling, and in situ DRIFTS measurements confirm the origin of products and validate the proposed catalytic pathways, including the associated oxidation half-reaction.

#### CRediT authorship contribution statement

**Chaitanya B. Hiragond:** Conceptualization, Methodology, Investigation, Formal analysis, Writing – original draft, review & editing;

**Prabhat Prakash:** Formal analysis, Validation, Writing – original draft, review & editing; **Tridip Das:** Formal analysis. **Niket S. Powar:** Formal analysis; **Eunhee Gong:** Formal analysis; **Jeonghyeon Lee:** Formal analysis; **Jin-Woo Jung:** Formal analysis; **Chang-Hee Cho:** Formal analysis; **William A. Goddard III:** Writing – original draft, review & editing, Supervision, Funding acquisition; and **Su-Il In:** Writing – original draft, review & editing, Supervision, Funding acquisition.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence

the work reported in this paper.

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## Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.apcatb.2026.127142](https://doi.org/10.1016/j.apcatb.2026.127142).

## Data availability

Data will be made available on request.

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