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Dual-temperature photothermal tandem catalysis for CO₂ conversion to olefins

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We report a dual-temperature photothermal tandem system that overcomes temperature mismatch for CO₂ hydrogenation to light olefins in a single reactor. A graphene-modified In₂O₃ top bed enables higher-temperature RWGS, and a K-doped Fe₂O₃ bottom bed facilitates lower-temperature FTS. This vertical configuration couples the two reactions, achieving a light-olefin production rate of 52.1 μmol g⁻¹ h⁻¹ with 69% selectivity at 0.05 MPa without external heating.

The increasing atmospheric CO₂ level is aggravating climate change and energy insecurity, highlighting the urgent need for sustainable carbon-recycling technologies.^{1,2} Among the various strategies, photothermal CO₂ reduction has attracted growing attention because it does not require external electrical input and enables full-spectrum solar utilization to activate inert CO₂ molecules.^{3,4} Significant progress has been achieved in CO₂ hydrogenation to C₁ products such as CH₄, CO, and CH₃OH.^{5,6} However, overcoming the kinetic barriers associated with C–C bond formation to directly produce C₂⁺ hydrocarbons remains highly challenging.^{7,8}

For thermocatalytic CO₂ hydrogenation towards C₂⁺ products, two tandem strategies are most frequently explored. One approach involves coupling CO₂-to-methanol with a subsequent methanol-to-olefins (MTO) process.^{9,10} Although this route can yield light olefins, methanol selectivity is highly pressure-dependent. It typically requires elevated pressures to suppress methanol decomposition, which is unfavourable for scalable operations under photothermal conditions. Another widely studied route converts CO₂ to CO *via* the reverse water-gas shift (RWGS) reaction, followed by Fischer–Tropsch synthesis (FTS) to form hydrocarbons.^{11–13} Integrating RWGS and

FTS in a single reactor is intrinsically difficult because the two steps require different optimal temperature windows: RWGS is endothermic and favours high temperatures >400 °C for efficient CO formation,^{14,15} whereas FTS requires moderate temperatures (200–350 °C) to promote C–C coupling and avoid excessive methane formation.^{16,17} This fundamental temperature mismatch is a key limitation to achieving direct CO₂-to-olefin conversion in a single photothermal reactor.

Compared with the recently reported single-reactor tandem photothermal system,¹⁸ this work employs a dual-bed reactor in which the RWGS and FTS functions are spatially separated. This design enables cascade heat utilization, suppresses local overheating, and allows independent optimization of each catalytic bed for improved flexibility in tuning target products. The top layer, made of graphene-modified In₂O₃ (G–In₂O₃), exhibits excellent photothermal conversion and efficiently reduces CO₂ to CO while simultaneously heating the gas phase and transferring heat to the downstream bed *via* combined radiative and convective heat transfer. This controlled heat flow determines the lower temperature of the potassium-doped Fe₂O₃ (K–Fe₂O₃) bed, where CO undergoes FTS to produce light olefins with high selectivity. The vertically stacked configuration establishes a well-defined temperature gradient, enabling the RWGS and FTS stages to operate within their respective optimal temperature ranges. Under low pressure (0.05 MPa), the tandem system achieves a light-olefin production rate of 52.1 μmol g⁻¹ h⁻¹ with 69% selectivity, demonstrating that engineering a temperature gradient is an effective strategy to overcome the inherent temperature mismatch in tandem photothermal catalysis.

The G–In₂O₃ composite in the top bed was prepared by using the hydrothermal method. The average particle size of In₂O₃ particles is 50–100 nm, and they are uniformly dispersed on the graphene sheets (Fig. S1). The high-resolution transmission electron microscopy (HRTEM) image (Fig. 1a) shows a distinct interface between graphene and In₂O₃. The corresponding fast Fourier transform patterns provide atomic-resolution structural information: the cubic lattice spots can be assigned to In₂O₃, while the hexagonal pattern arises from the characteristic six-fold

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Fig. 2 (a) Effect of the integration mode of G-In₂O₃-10% and K-Fe₂O₃-5% (mass ratio 3 : 5) on hydrocarbon distribution and light-olefin production rate under identical photothermal CO₂ hydrogenation conditions. (b) Time profiles of CO₂, CO, C₂H₄ and C₃H₆ over the dual-bed G-In₂O₃-10%/K-Fe₂O₃-5% catalyst under continuous illumination. (c) The UV-Vis-NIR spectra of graphene, In₂O₃ and G-In₂O₃-10%. (d) Time evolution of the surface temperature of the G-In₂O₃-10% and K-Fe₂O₃-5% beds.

confirming that efficient tandem CO₂ reduction and F-T coupling require the correct thermal and reactant-flow sequence. This improvement arises from the temperature distribution and reaction dynamics revealed in Fig. 2b. In the dual-bed configuration, the upper G-In₂O₃-10% layer, operating at a higher photothermal temperature, rapidly converts CO₂ to CO and steadily increases the CO concentration throughout the reaction (Fig. 2b). As CO continues to accumulate, the concentration surpasses the threshold required to trigger chain-growth reactions in the downstream FTS bed. Olefin production begins to rise significantly after 120 min and continues to increase over time. Meanwhile, the CO formation rate gradually approaches a quasi-steady state, while CO₂ is continuously consumed. These results demonstrate that the upper G-In₂O₃ bed must supply CO with high selectivity and rate to initiate and sustain FTS in the lower K-Fe₂O₃ bed, thereby enabling efficient tandem photothermal CO₂-to-olefin conversion. Detailed analysis of the stability test is provided in Fig. S15 of the SI.

As a result, the photothermal conversion efficiency of the upper G-In₂O₃ layer is crucial. The light source primarily irradiates the top bed containing G-In₂O₃. G-In₂O₃ was selected because the tandem process is initiated by light-driven RWGS, which produces CO as the key intermediate for the subsequent FTS reaction in the lower bed. Positioning In₂O₃ in the upper bed promotes the formation of a CO-rich stream under continuous unidirectional gas flow. Moreover, UV-Vis-NIR spectra (Fig. 2c) show that pristine In₂O₃, as a wide-band-gap semiconductor (3.2 eV, Fig. S16), shows weak absorption across visible and near-infrared regions. Graphene endows G-In₂O₃ with strong, nearly broadband light absorption, enabling efficient photothermal conversion. The heat generated in the upper bed can also be transferred to the downstream K-Fe₂O₃ bed through thermal radiation and gas-phase convection, helping to maintain the temperature required for the tandem reaction. The

resulting thermal distribution in the dual-bed configuration is confirmed under photothermal operation (Fig. 2d): the upper G-In₂O₃ layer rapidly reaches ~360 °C within 10 min, while the lower K-Fe₂O₃ layer stabilises at ~260 °C. The respective temperatures also precisely correspond to the optimal adsorption range (Fig. S17).²⁷

To identify the active sites in G-In₂O₃ for CO₂ reduction, XPS and EPR measurements were carried out. In comparison, the corresponding peaks of G-In₂O₃ shift to lower binding energies, which can be attributed to electron transfer at the graphene/In₂O₃ interface and an increased concentration of oxygen vacancies (Fig. 3a). The O 1s spectra (Fig. 3b) can be deconvoluted into two contributions: the peak at 529.8 eV is assigned to lattice oxygen in In-O-In, whereas the peak at 531.4 eV is associated with oxygen vacancies.²⁸ Furthermore, the stronger EPR signal for G-In₂O₃ shows that it has a higher oxygen-vacancy level (Fig. 3c),²⁹ aligning with the XPS results. This suggested that carbon at the graphene/In₂O₃ interface lowers the energy needed to create oxygen vacancies in the In₂O₃ lattice.

Because the oxygen vacancy concentration evolves under photothermal reaction conditions, we compared the XRD, PL, EPR and UV-vis-NIR spectra of G-In₂O₃ before and after the reaction (Fig. S18–S21). Detailed characterization and analysis are provided in the SI.

Regarding the active phase of the K-Fe₂O₃ catalyst in the FTS reaction, XPS measurements were carried out to determine the surface elemental composition and chemical states (Fig. 3d). In the Fe 2p spectrum, upon K promotion, the Fe 2p_{3/2} peak shifts to a lower binding energy, indicating a more reduced Fe environment and thus facilitating the transformation of Fe species into Fe₅C₂, which is widely recognised as the active phase for FTS in Fe-based catalysts.^{30–32} In the C 1s spectrum (Fig. 3e), three C 1s components together with an additional K 2p signal are observed. Compared with pristine Fe₂O₃, the K-Fe₂O₃ sample



Fig. 3 The XPS spectra of (a) In 3d and (b) O 1s, (c) the EPR spectra of G-In₂O₃-10% and In₂O₃, the XPS spectra of (d) Fe 2p and (e) C 1s, (f) the XRD patterns of K-Fe₂O₃-5% and Fe₂O₃, (g) the *in situ* FTIR spectra of G-In₂O₃-10% and K-Fe₂O₃-5%, and (h) the advance and process of the photothermal CO₂ reduction to light olefins.



exhibits new carbide-related C 1s features, aligning with the leftward shift of the Fe 2p_{3/2} peak.³³ XRD patterns of Fe₂O₃ and K-Fe₂O₃ (Fig. 3f) further reveal that additional reflections in K-Fe₂O₃ can be indexed to the main diffraction peaks of Fe₅C₂, with no Fe₃C phase detected (Fig. S22).^{34,35} K doping plays multiple roles in the Fe-based catalyst by enhancing CO adsorption and activation, increasing chain-growth probability, and suppressing the secondary hydrogenation of olefins, thereby improving light-olefin selectivity. In addition, K facilitates the formation and stabilization of the Fe₅C₂ active phase, which contributes to the enhanced FTS performance.³⁶

Although In₂O₃ is widely recognized as an effective catalyst for CO₂ hydrogenation to methanol under relatively high pressures, the reaction in this work was performed at 0.5 atm, which is less favorable for methanol formation.³⁷ To elucidate the CO₂ activation pathway, *in situ* FTIR spectroscopy was conducted (Fig. 3g). The spectra show a band at 1398 cm⁻¹ assigned to carbonate species and a band at 1560 cm⁻¹ attributed to COOH* intermediates. Since COOH* species are generally associated with the RWGS pathway to CO rather than the methanol pathway *via* HCOO*, these results indicate that CO is the predominant product in the present system. The feature at 1634 cm⁻¹ originates from adsorbed water, and the bands at 2114 and 2171 cm⁻¹ are ascribed to linearly and bridge-bonded adsorbed CO*, respectively. The band at 2917 cm⁻¹ is characteristic of CH₃* species, and the broad absorptions at 3417 and 3724 cm⁻¹ are associated with surface hydroxyl groups and adsorbed water molecules.³⁸ Accordingly, these surface intermediates provide direct spectroscopic evidence for a tandem RWGS-FTS mechanism, wherein CO₂ is first reduced to CO *via* RWGS, and then the resulting CO is subsequently hydrogenated through CH_x* intermediates to form light hydrocarbons.³⁹⁻⁴¹

In summary, we have developed a tandem dual-temperature catalytic configuration that enables controlled multi-stage temperature distribution and efficient energy utilisation for the photothermal hydrogenation of CO₂ into high-value hydrocarbons. In the upper bed, G-In₂O₃ drives the RWGS reaction. The absorbed light energy is converted into heat and transmitted to the underlying K-Fe₂O₃ bed *via* both radiative and convective heat transfer. In the lower bed, K-Fe₂O₃ drives the FTS process (Fig. 3h). By synergistically engineering the dual-bed catalysts with optimal operational temperatures in a single photothermal reactor, we achieve direct CO₂-to-light-olefin conversion with a production rate of 52.1 μmol g⁻¹ h⁻¹ and a selectivity of 69%, demonstrating a promising strategy for solar-driven CO₂ valorisation.

Z. L.: Investigation, Methodology, Writing – original draft. L. H. and C. Z.: Formal analysis, Data curation. Z. Y. and Z. W.: Investigation, Validation, Visualization. Y. Q.: Conceptualization, Supervision, Project administration. S. X.: Conceptualization, Writing – review & editing.

Conflicts of interest

There are no conflicts to declare.

Data availability

Data will be made available on request. Supplementary information is available. See DOI: <https://doi.org/10.1039/d5cc07291c>.

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