School of Chemical Engineering

A Step Towards Sustainable Future: The Low Temperature Photo-enhanced Storage of H2 as CH4 using Co- La/TiO2 Catalysts

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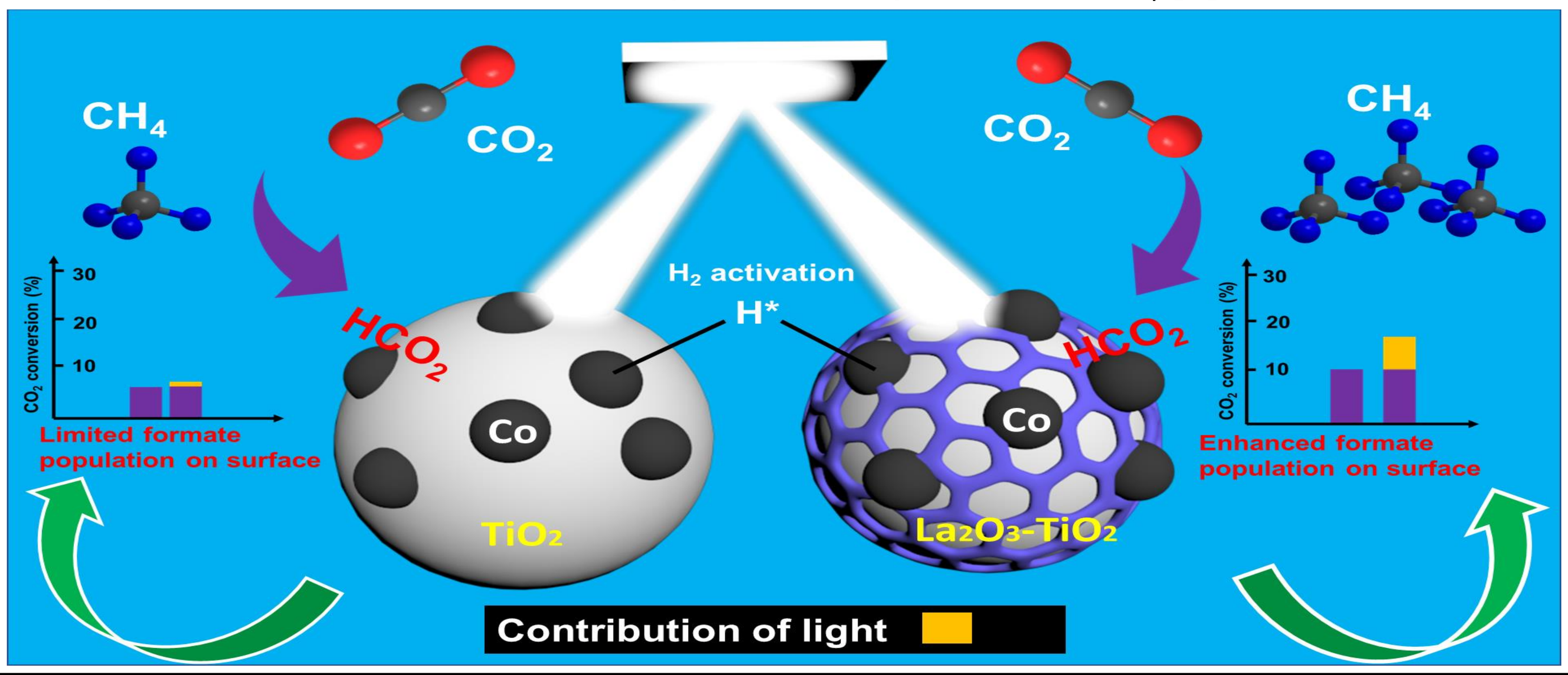
Aims

- Achieve low temperature storage of H_2 as CH_4 using abundant Solar energy.
- Understand the role of plasmonic metal under visible light illumination for hydrogenation of CO_2 to CH_4, a potential renewable H_2 carrier.
- Understand the role of basic support under light illumination.
- Compare the CO_2 conversion and CH_4 selectivity under dark and illuminated conditions by varying surface basicity.

Background and Motivation

- CO_2 concentration in atmosphere is increasing.
- Sabatier reaction: $CO_{2(g)} + 4H_{2(g)} \rightarrow CH_{4(g)} + 2H_2O_{(g)}$ $\Delta H = -165.0$ kJ/mol
- Synthetic CH_4 is an appealing solution for H_2 management due to presently available CH_4 storage and transportation infrastructure.
- Kinetic limitations due to CO_2 stability [1].
- Driving force- Solar energy as an alternative approach.
- Light: Facilitation of intermediary/reactive species to CH_4 [2].



Methodology

Catalyst Synthesis
10% Co/xLa-TiO$_2$ (x= 0, 5, 10,15) prepared via wet impregnation

→ **Characterizations**
H_2-TPR, XRD, BET, ICP-OES, UV Vis, DRIFTS

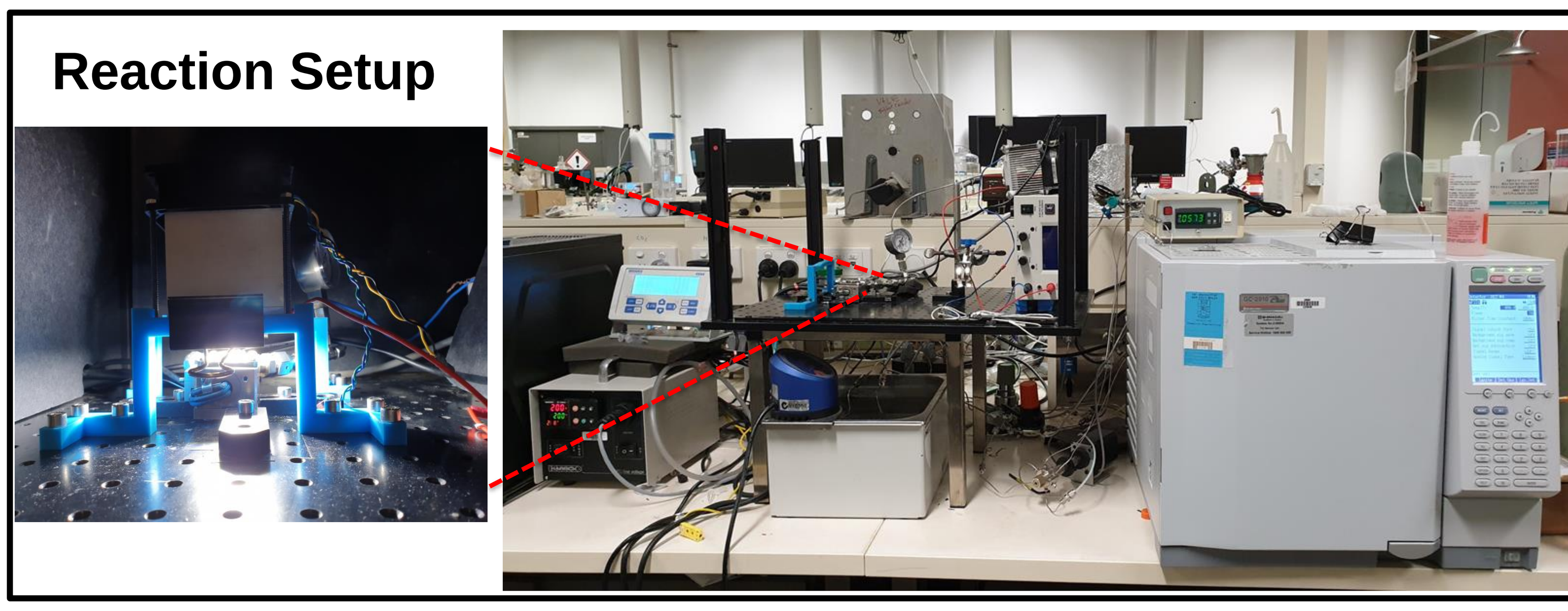
Pre-Reaction reduction
Reduced with N_2/H_2 at 500 °C for 2h

→ **Thermal Evaluation Test**
- 45 mg catalyst
- 150 °C to 450 °C CO_2:H_2:N_2 (1:4:1, 24 mL min^{-1})
- N_2 as internal standard for GC (4 mL min^{-1})

Light Illumination Test
- 45 mg catalyst
- 150 °C to 450 ° C CO_2:H_2 :N_2 (1:4:1, 24 mL min^{-1})
- Light Intensity 0.5 W/cm^2
- White LED (λ = 300-780 nm)

→ **Analysis**
CO_2 (X), CH_4 (S), XRD, CO_2 TPD, Relative reducibility

Reaction Setup



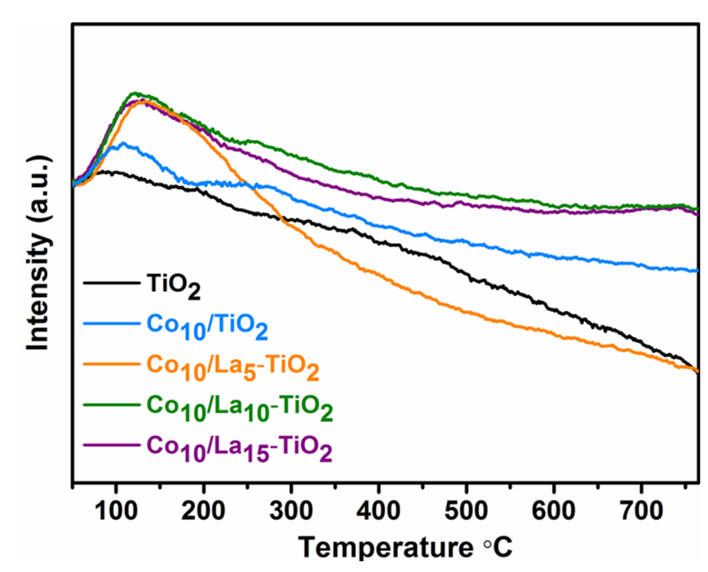
Results & Discussion

Catalyst Properties

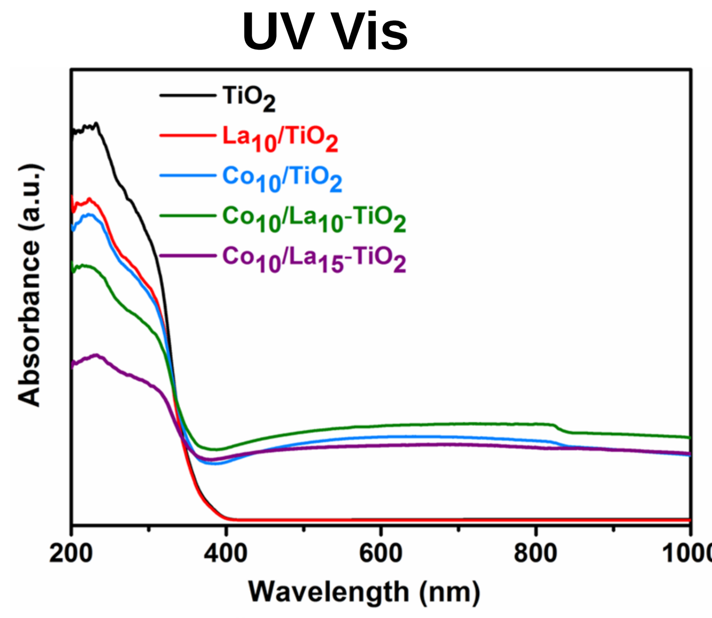
Sample	La_2O_3 loading [a] (wt.%)	Co loading [a] (wt.%)	S_{BET} [b] (m²/g)	Co crystallite size [c] (nm)
TiO_2	-	-	65	-
La_{10}/TiO_2	9.5	-	58	-
Co_{10}/TiO_2	-	9.2	54	19.4
Co_{10}/ La_5-TiO_2	4.5	9.9	54	17.5
Co_{10}/ La_{10}-TiO_2	9.4	9.7	55	12.3
Co_{10}/ La_{15}-TiO_2	14.3	9.6	45	13.0

a. Determined by ICP-OES b. Determined by BET calculation c. Determined by XRD using the Scherrer equation

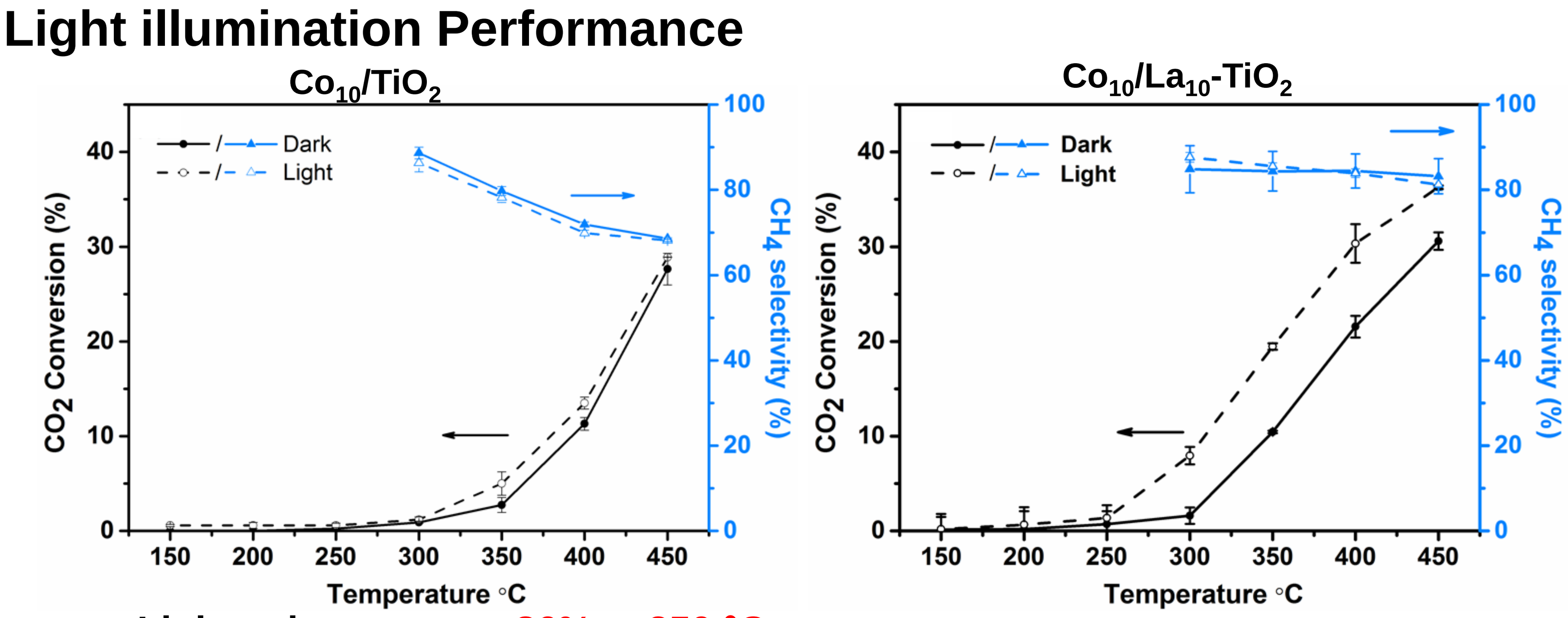
CO2 TPD



UV Vis

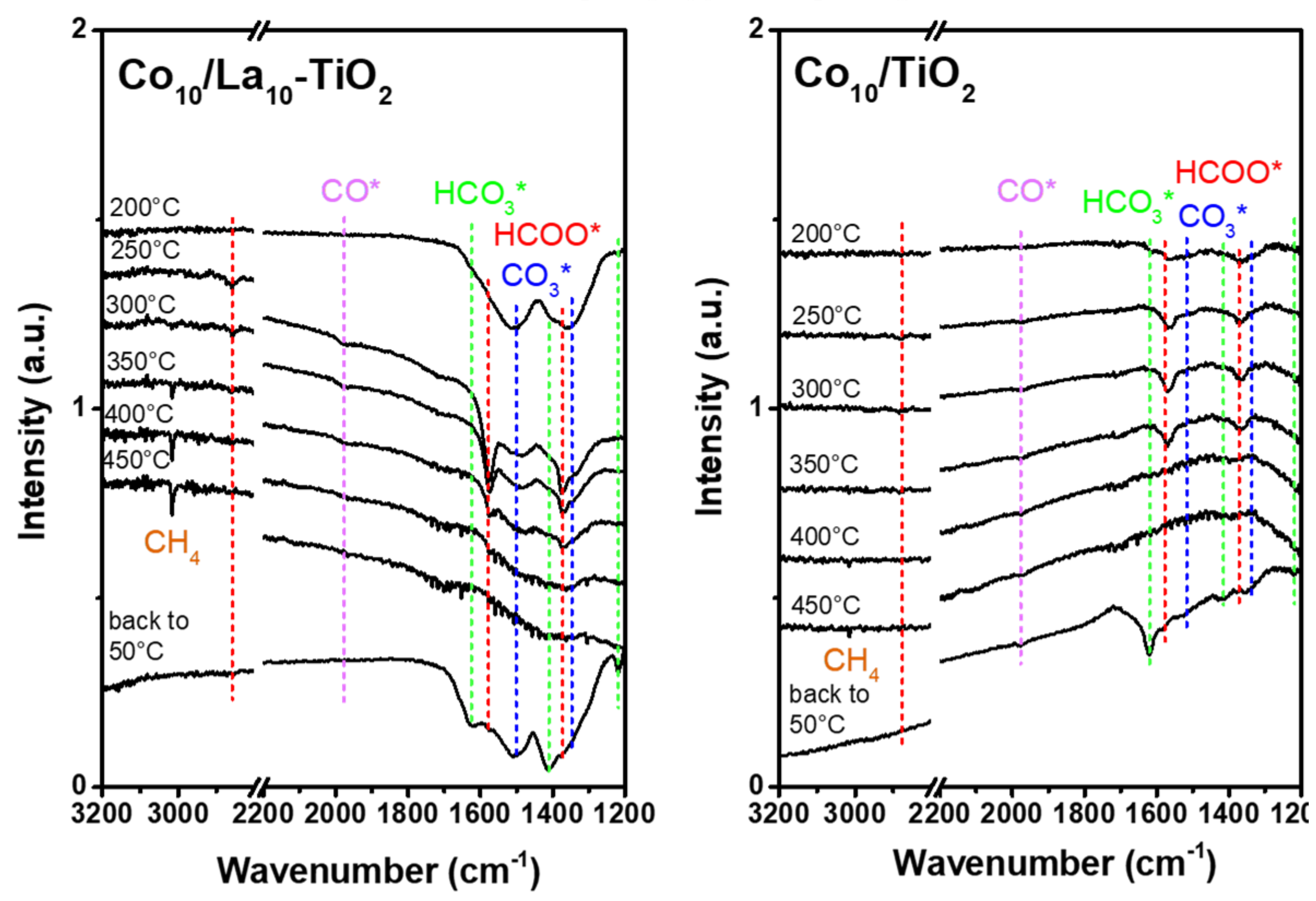


Light illumination Performance



- **Light enhancement: 86% at 350 °C**
- **Selectivity: > 80 %**
- **Stability: 10 h**

In-situ DRIFTS



- HCOO* species formation governs catalyst performance

Conclusions

- Light illumination lowered activation energy by 20% and increased conversion by 86% at 350°C.
- Transition metals with broader plasmonic response can potentially hydrogenate CO_2 to CH_4 using visible range energy of Solar spectrum.
- La promotion decreased Co crystallite size and improved surface basicity on TiO_2.
- La facilitated the adsorption of CO_2 and its transformation to HCOO* species susceptible to light
- Enhancement.
- Solar energy being an important global energy mix facilitate hydrogenation reactions –a step towards a sustainable solution.

References

[1] Chen, G.; Waterhouse, G. I. N.; Shi, R.; Zhao, J.; Li, Z.; Wu, L. Z.; Tung, C. H.; Zhang, T. From Solar Energy to Fuels: Recent Advances in Light-Driven C1 Chemistry. Angew. Chemie - Int. Ed. 2019, 58 (49), 17528–17551.

[2] Kim, C.; Hyeon, S.; Lee, J.; Kim, W. D.; Lee, D. C.; Kim, J.; Lee, H. Energy-Efficient CO2 Hydrogenation with Fast Response Using Photoexcitation of CO2 Adsorbed on Metal Catalysts. Nat. Commun. 2018.