Methane to Products:
A Sustainable Path to Methane Conversion by Advanced Electrochemical Technologies

Photocatalytic coupling of methane over TiO_2/WO_3 heterojunction photocatalysts to enhance the production of ethane and hydrogen

***S.A. Carminati*, J. M. Vaz, E. V. Spinacé**

Instituto de Pesquisas Energéticas e Nucleares, IPEN/CNEN, Av. Prof. Lineu Prestes, 2242 – Cidade Universitária, São Paulo, SP, 055008-000, Brazil

saulocarminati89@gmail.com

Introduction

Methane (CH_4), as the principal constituent of natural gas, has been recently used as a fuel and is an important raw material in many industrial chemical processes. By employing efficient photocatalysts with appropriate active sites, methane conversion reactions that are thermodynamically unfavorable can be feasibly mediated by solar energy and produce high chemical potential products.[1] The incorporation of alternative semiconductors such as WO_3 may synergistically improve the photocatalytic efficiency of TiO_2 under visible light irradiation, resulted from optical and electronic properties modification.[2] We have synthesized nanostructured TiO_2/WO_3 modified with platinum nanoparticles towards CH_4 coupling to produce ethane (C_2H_6) and hydrogen (H_2) from water splitting. By loading with Pt nanoparticles, the C_2H_6 production rate increased from 80 to 180 µmol h^{-1} g^{-1}. The TiO_2/WO_3/Pt heterostructure achieved H_2 production rate of 2478 µmol h^{-1} g^{-1}. This can be assigned to efficient charge transfer by the formation of the heterojunction, while the Pt nanoparticles enhanced the electron collection to reduce H^+ to H_2.

Methods

TiO_2 (P25)

↓

WO_3 impregnation (Na_2WO_4)

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Annealing → 500 °C /2 h

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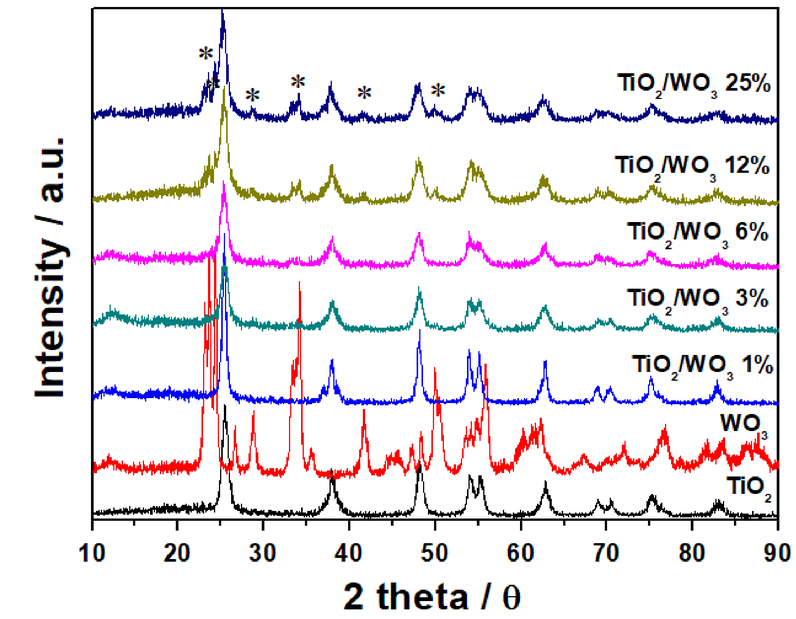
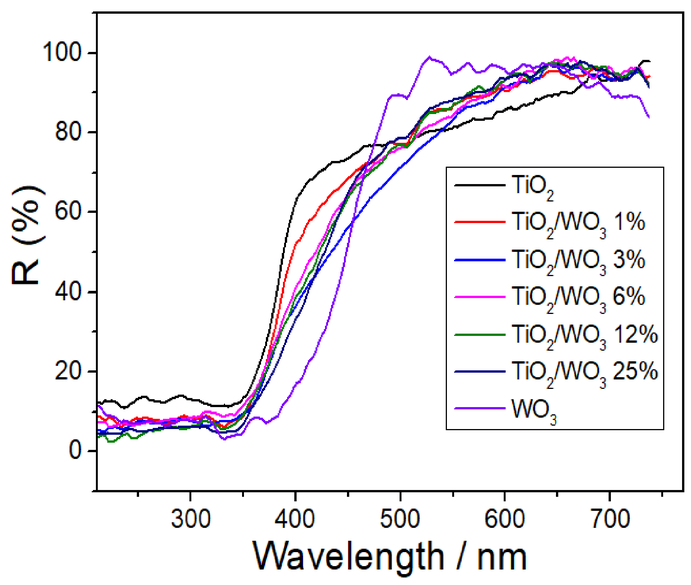
Pt deposition – Alcohol reduction method — Ethylene glycol + reflux

- CH_4 conversion in a flow reactor under mild conditions
- Quantification of the products (GC-MS)

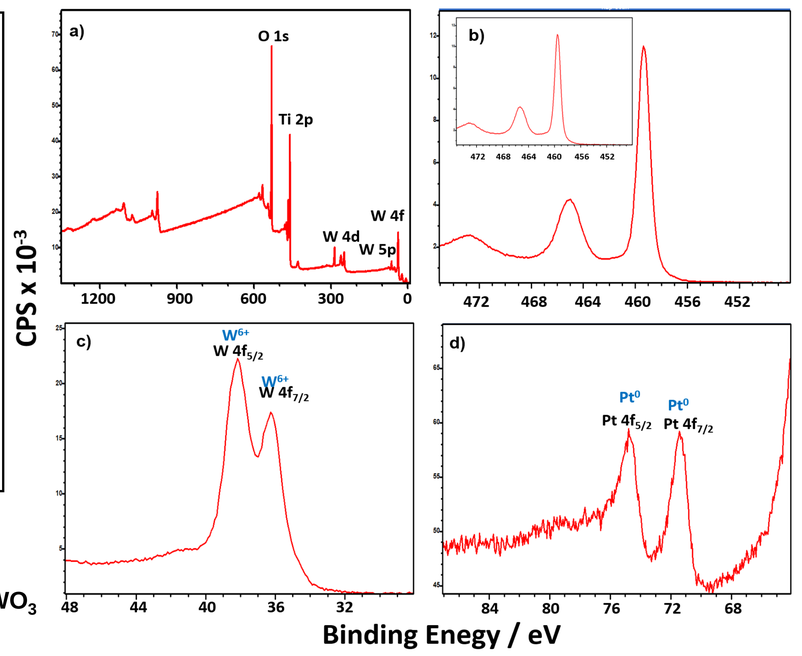
Results



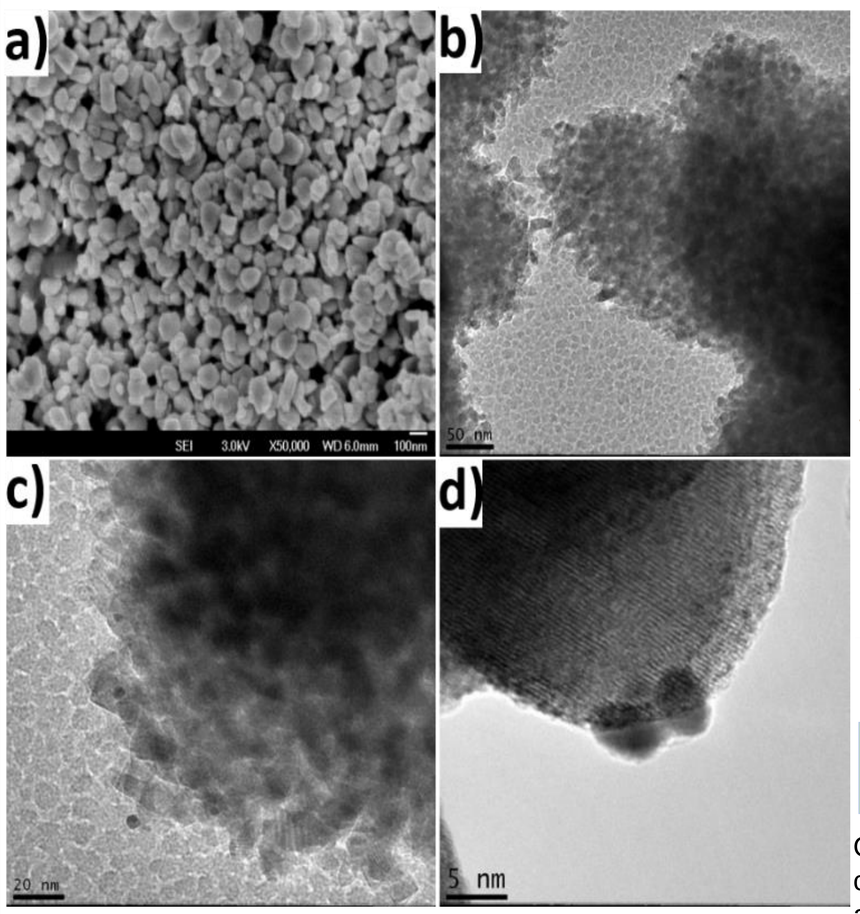
XRD patterns of TiO_2, WO_3 and TiO_2/WO_3 photocatalysts varying the concentration of WO_3.



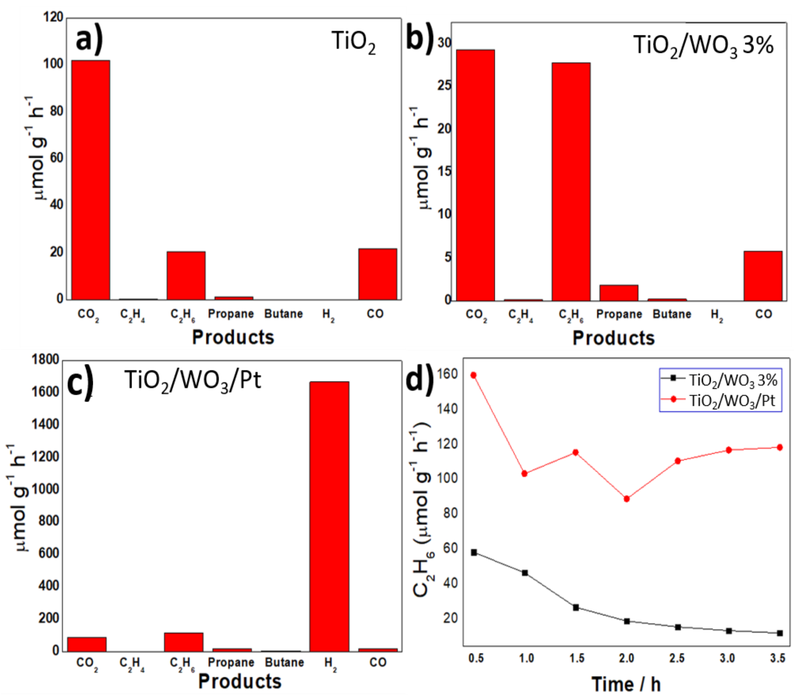
Diffuse reflectance spectra of TiO_2, WO_3 and TiO_2/WO_3 photocatalysts varying the concentration of WO_3.



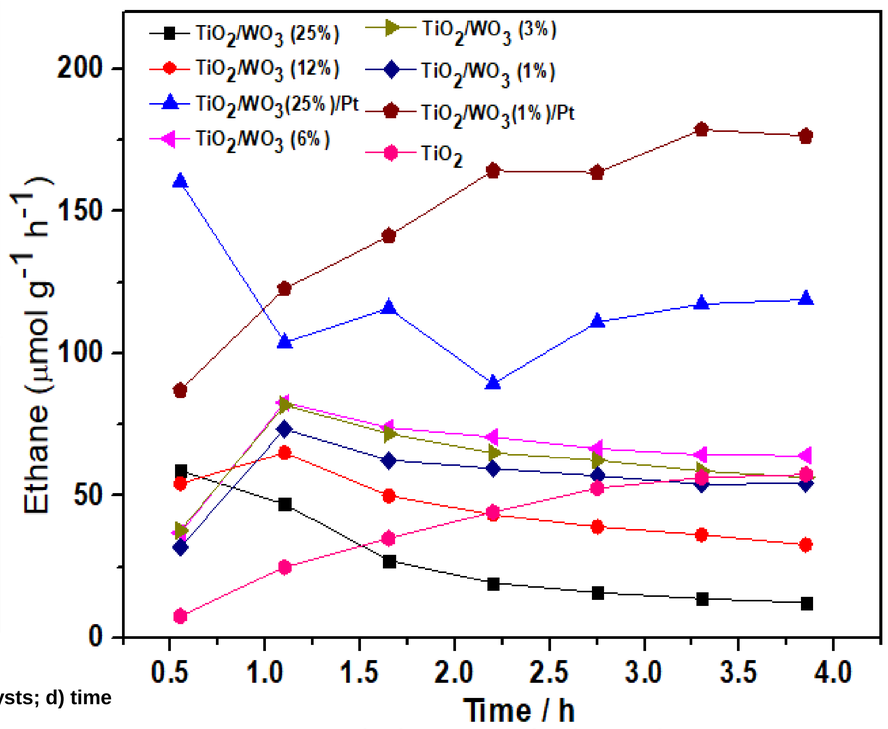
XPS spectra of TiO_2/WO_3/Pt Photocatalyst: a) Typical survey, b)Ti 2p, c) W4f and d) Pt 4f.



TEM images of a) WO_3, b) TiO_2, c) TiO_2/Pt and d) TiO_2/WO_3/Pt photocatalysts.



Photocatalytic activities over a) TiO_2, b) TiO_2/WO_3 and c) TiO_2/WO_3/Pt photocatalysts; d) time course of C_2H_6 formation over TiO_2/WO_3 and TiO_2/WO_3/Pt photocatalysts.



C_2H_6 production rate over the photocatalysts.

Conclusions

Owing to the introduction of WO_3 and Pt, the TiO_2/WO_3/Pt heterojunction photocatalyst exhibited better performance over CH_4 conversion to C_2H_6 and H_2 compared to the pristine materials. This study showed that the presence of WO_3 in a low concentration is an efficient way to benefit the C_2H_6 formation rate due to better charge separation and by introducing Pt nanoparticles, H_2 generation was achieved. The synergistic effect between the materials contributed to the selective coupling of CH_4 and H_2 production.

References

1 - M. S. A. Sher Shah, C. Oh, H. Park, Y. J. Hwang, M. Ma and J. H. Park, *Adv. Sci.*, 2020, 7, 2001946.

2 - S. Y. Toledo Camacho, A. Rey, M. D. Hernández-Alonso, J. Llorca, F. Medina and S. Contreras, *Appl. Surf. Sci.*, 2018, **455**, 570-580

Acknowledgments

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