Influence of the Au particle size on the catalytic performance of plasmonic Au/TiO2 nanocatalysts in the sunlight-powered reverse water gas shift reaction

Jordi Volders[a], Ken Elen[a, b], Pegie Cool[c], Sammy Verbruggen[c], Francesc Sastre[d], Pascal Buskens[a, d], An Hardy[a, b], Marlies K. Van Bael[a, b]

[a] Institute for Materials Research; Design and Synthesis of Inorganic Materials (DESINe); Hasselt University; Agoralaan Building D; B-3590 Diepenbeek (Belgium) + Energyville; Thor Park 8310; 3600 Genk (Belgium)
[b] IMEC vzw; IMOMEC Associated Laboratory; Wetenschapspark 1; B-3590 Diepenbeek (Belgium)
[c] University of Antwerp, Groenenborgerlaan 171, 2020, Antwerp, Belgium
[d] The Netherlands Organisation for Applied Scientific Research (TNO); High Tech Campus 25; 5656AE Eindhoven (The Netherlands)

INTRODUCTION

Plasmon catalysis for endothermic reverse water-gas shift (rWGS) reaction making use of sunlight and renewable hydrogen is a low temperature alternative to the conventional thermal process.[1]

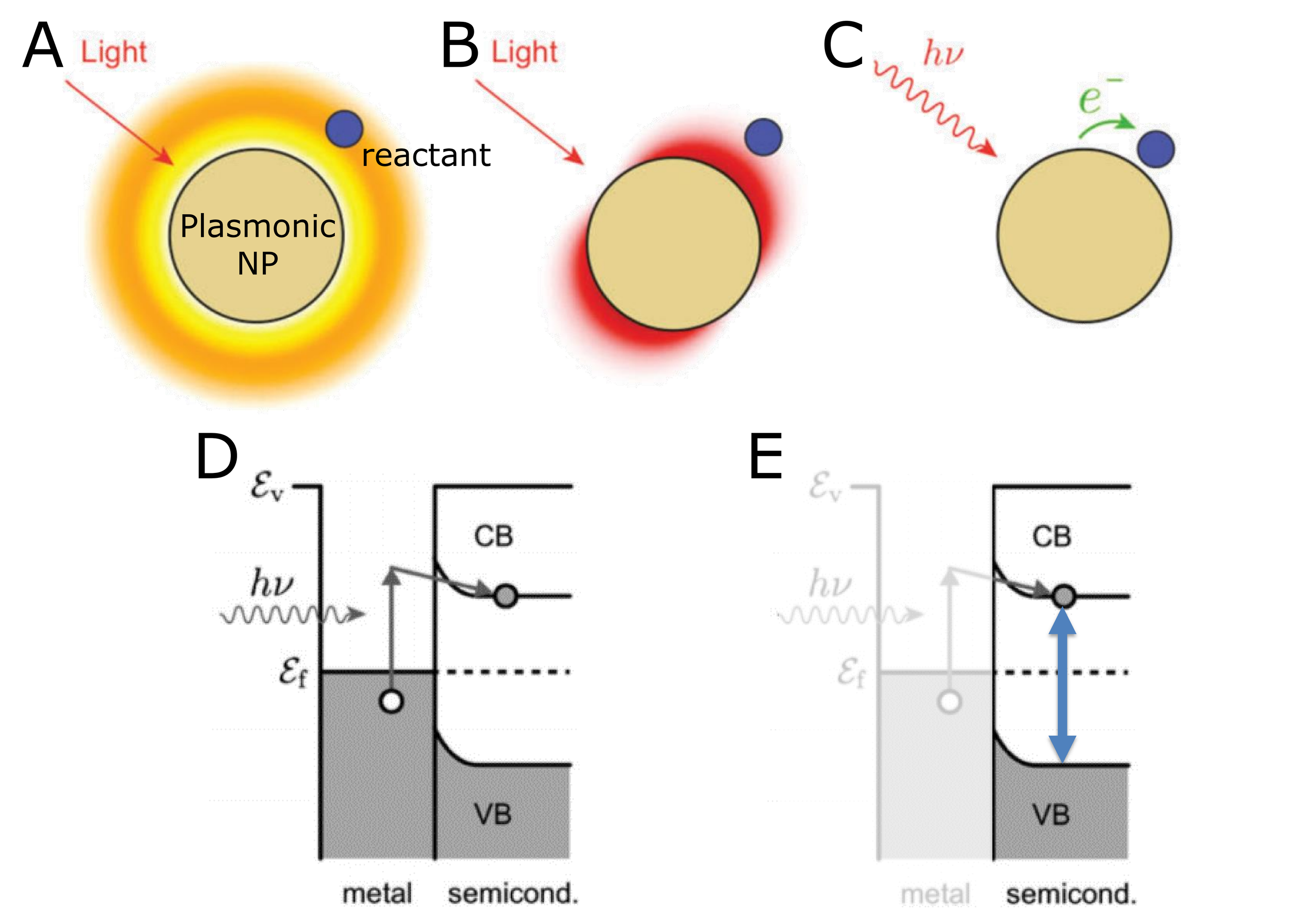
$$CO_2 + H_2 \rightleftharpoons CO + H_2O \quad \Delta H_r = 41.2 \text{ kJ mol}^{-1}$$

A plasmonic catalyst consists of plasmonic nanoparticles dispersed on a supporting oxide, which can be semiconducting or insulating. The plasmonic nanoparticles exhibits localised surface plasmon resonance (LSPR) upon illumination. This results in the catalyst exhibiting following pathways to catalyse reactions:[2]

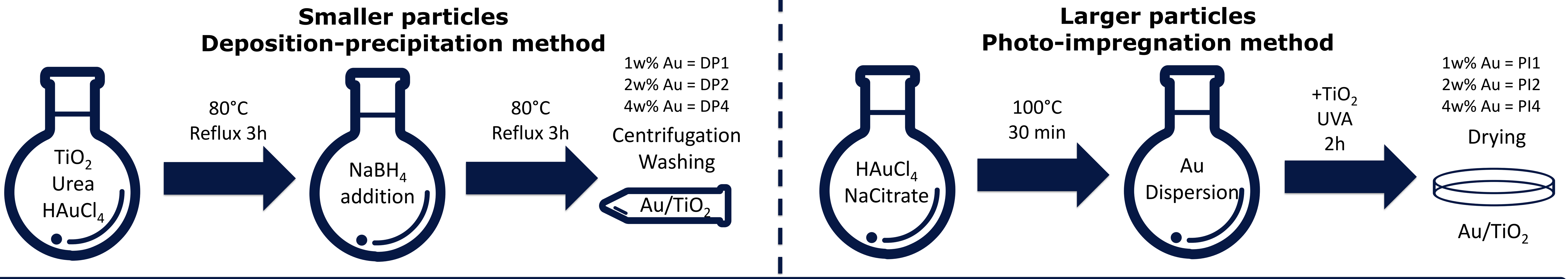
- Local heat generation (fig. A)
- Near field enhancement (fig. B)
- Hot electron injection (fig. C)
- Charge separation over Schottky barrier (if semiconducting support) (fig. D)
- Band gap activity of semiconductor (if semiconducting support) (Fig. E)

To investigate which catalytic effects contribute to rWGS reaction: Au was chosen as plasmonic nanoparticle for a high selectivity towards CO production and strong plasmonic resonance. P25 TiO_2 was chosen as semiconducting oxide with a band gap in the near UV and good photocatalytic properties.

In order to investigate the catalytic effects at play, as well as the impact of plasmonic nanoparticle size, smaller (5.5 nm) and larger (16 nm) particles were synthesised on the TiO_2 support and tested for catalytic activity in both light and dark conditions.

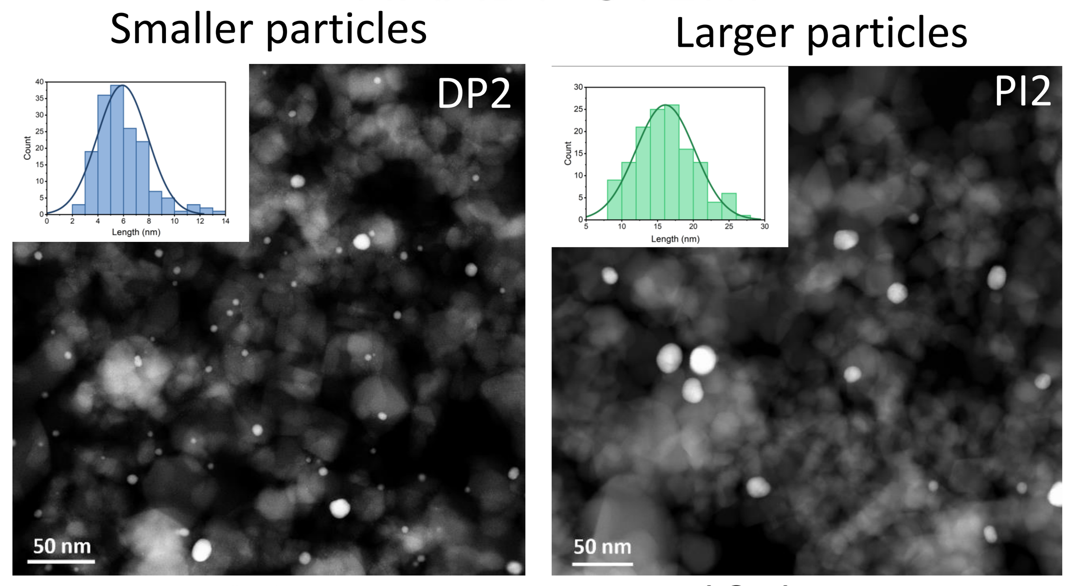


SYNTHESIS



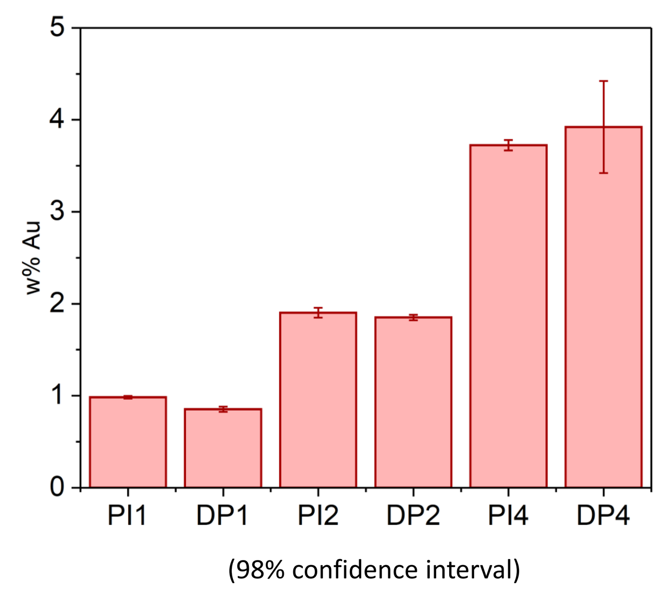
CHARACTERISATION

HAADF-STEM



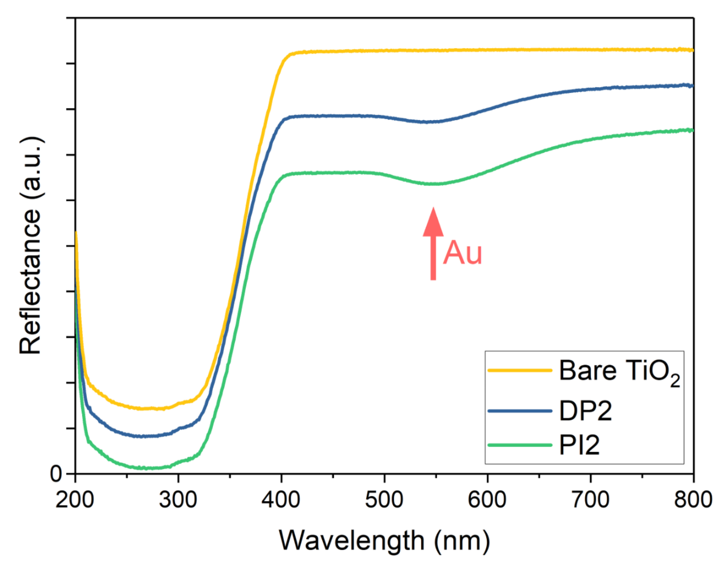
5.5±0.4 nm (98% confidence interval) 16±1 nm

ICP-AES

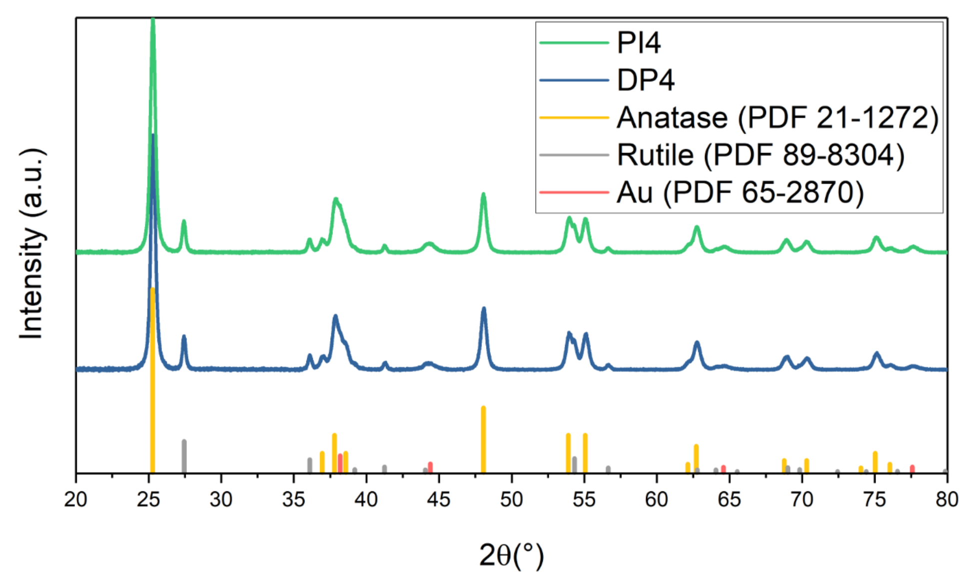


(98% confidence interval)

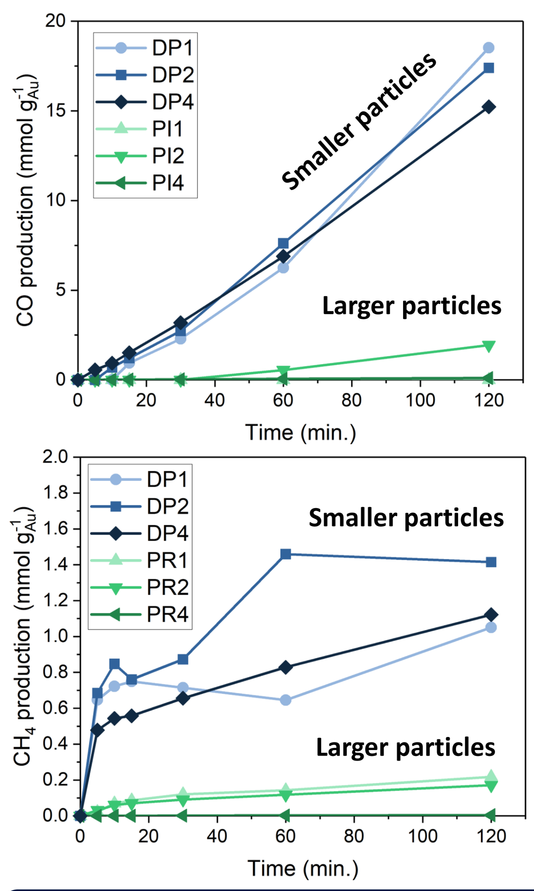
UV-vis



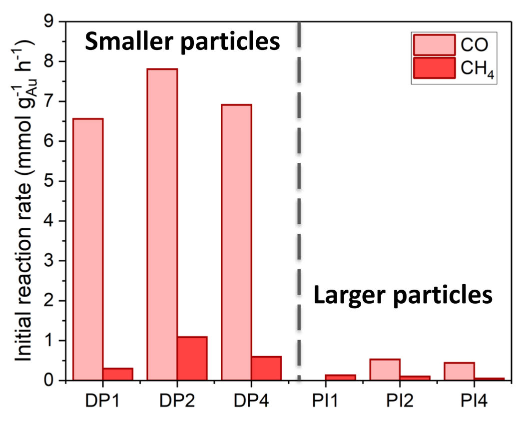
XRD

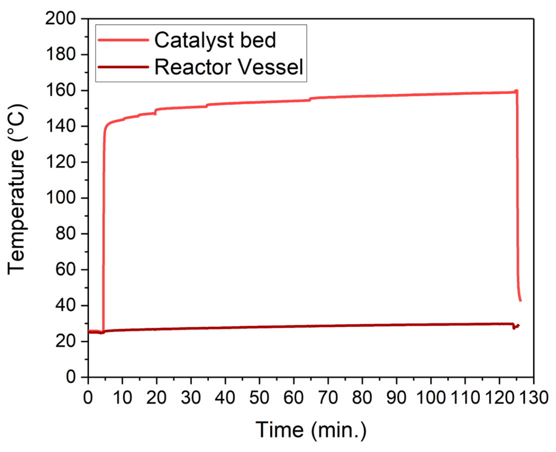


CATALYTIC PERFORMANCE



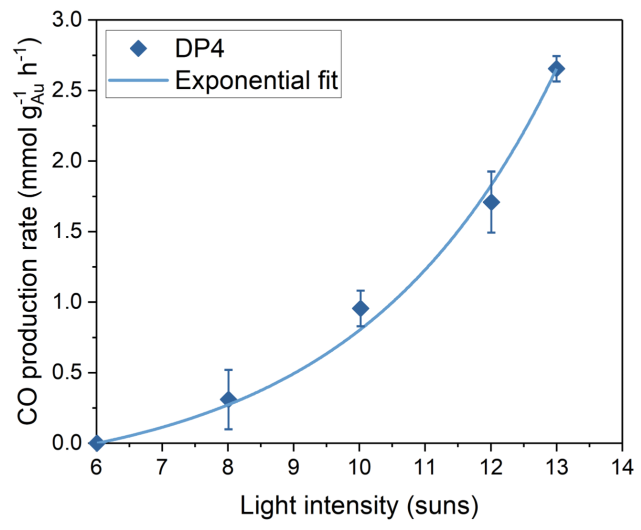
14 sun
No external heating





Selective CO formation

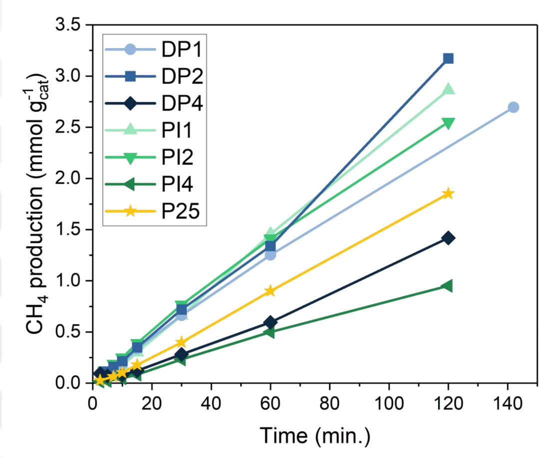
Light variation
No external heating

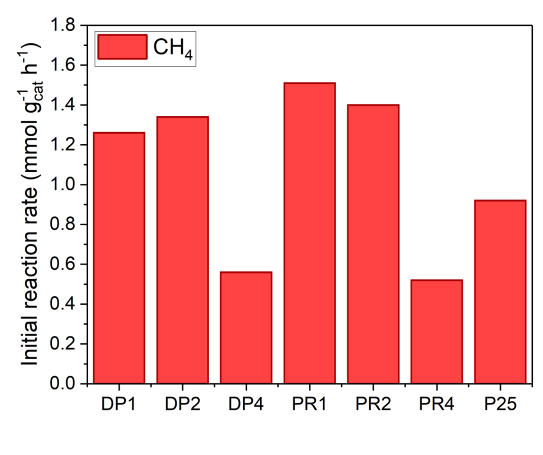


Selective CO formation

(98% confidence interval)

Dark
160°C external heating





Selective CH_4 formation

CONCLUSIONS

→ Small and large Au/TiO_2 synthesised. Optical and physical properties characterised.
→ **Higher CO selectivity and activity for smaller nanoparticles → larger surface area and more plasmonic absorption.**
→ Light variation experiments show that the plasmonic activated rWGS reaction is photothermally driven.
→ In dark reference experiments, only CH_4 production was observed, indicating the presence of a photochemical aspect.
→ **Enhanced CO desorption through plasmonic generated charge-carriers, switching the selectivity towards rWGS reaction.**

REFERENCES

[1]Kaiser, P., et al., Production of Liquid Hydrocarbons with CO2 as Carbon Source based on Reverse Water-Gas Shift and Fischer-Tropsch Synthesis. Chemie Ingenieur Technik, 2013. 85(4): p. 489-499.

[2]Baffou, G. and R. Quidant, Nanoplasmonics for chemistry. Chemical Society Reviews, 2014. 43(11): p. 3898-3907.

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ACKNOWLEDGEMENTS

FLANDERS INDUSTRY INNOVATION MOONSHOT
AGENTSCHAP INNOVEREN & ONDERNEMEN
IMO-IMOMEC
UHASSELT
imec
Universiteit Antwerpen
EnergyVille