Understanding the catalytic activity of plasmonic gold on ceria for the reverse water-gas shift conversion of CO_2

Jordi Volders[a], Ken Elen[a, b], Pascal Buskens[a, c], 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] The Netherlands Organisation for Applied Scientific Research (TNO); High Tech Campus 25; 5656AE Eindhoven (The Netherlands)

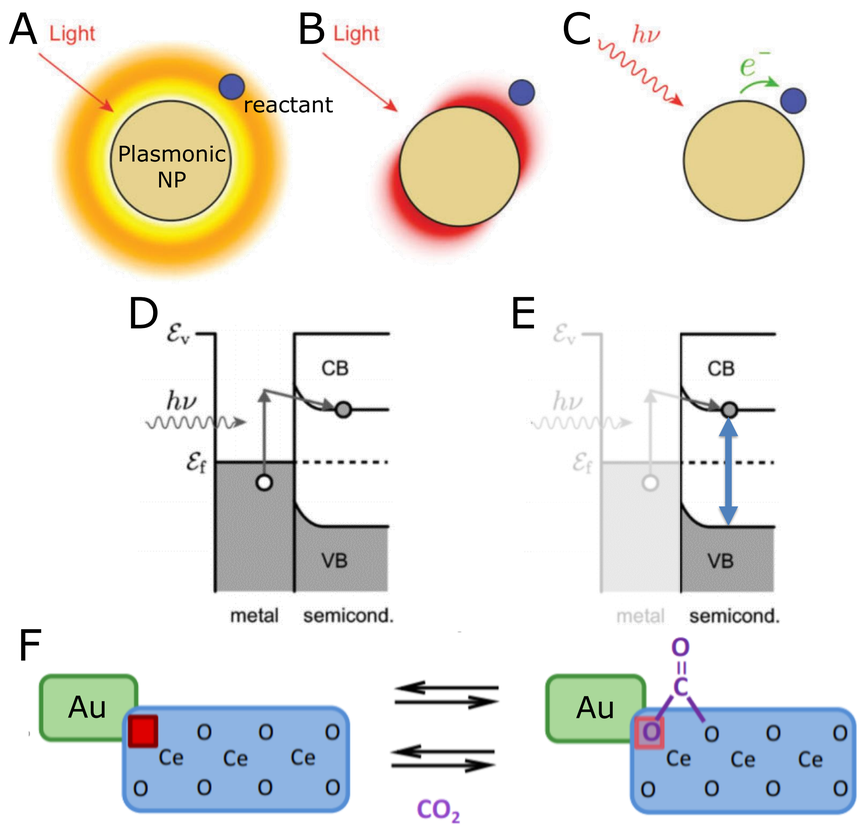
Introduction

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]

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

Plasmonic catalyst consists of plasmonic nanoparticle dispersed on semiconducting oxide. Plasmonic nanoparticle 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 (fig. D)
- -Band gap activity of semiconductor (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. CeO_2 was chosen as semiconducting oxide with a band gap in the near UV and high CO_2 adsorption. Oxygen vacancies can be generated in vicinity of plasmonic nanoparticles as shown in fig. F.[3] The amount of oxygen vacancies could be tuned to increase local CO_2 adsorption.

In order to investigate the catalytic effects, first a strong foundation must be built: A flexible, reproducible synthesis route for the CeO_2 support must be defined; The ability to tune oxygen vacancy content within the support must be investigated; Au deposition on the support must be homogenous and result in a good metal-semiconductor contact; The synthesised catalyst should be catalytically active in the reactor.

Experimental

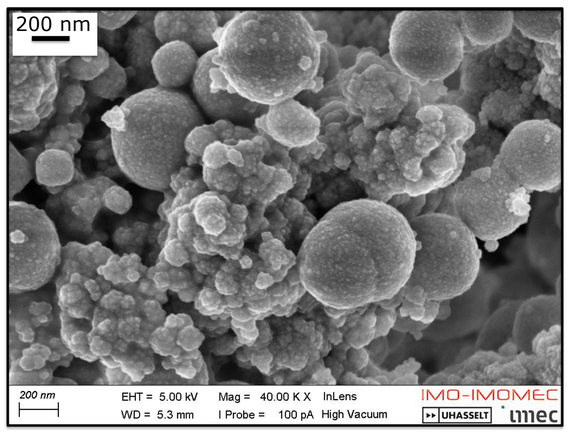
Results

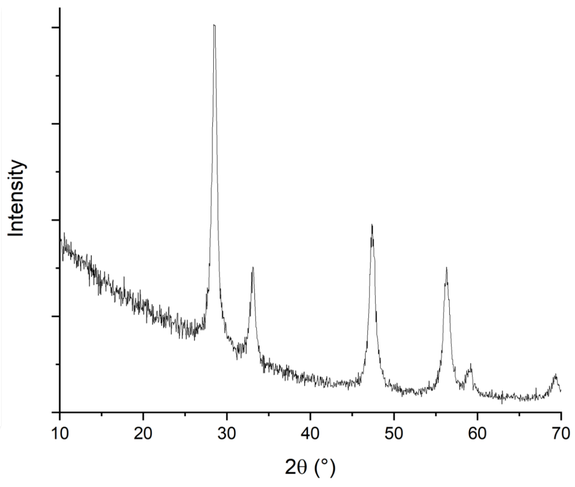
CeO_2 characterisation

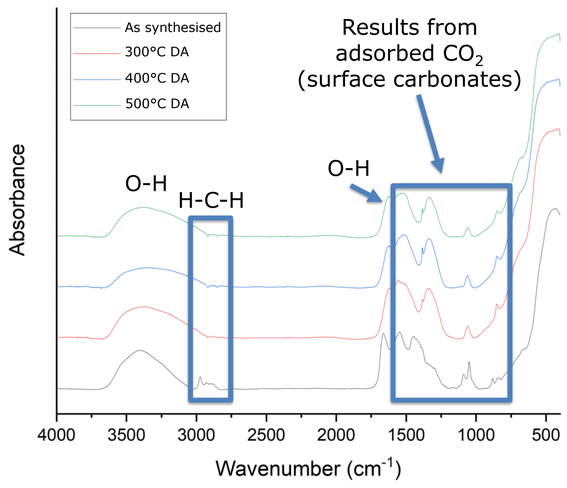
Size and morphology:
→ Crystallites in spherical amorphous matrix

Crystallinity:
→ Fluorite crystal structure observed

Organic residuals from synthesis:
→ Calcination in air removes PVP

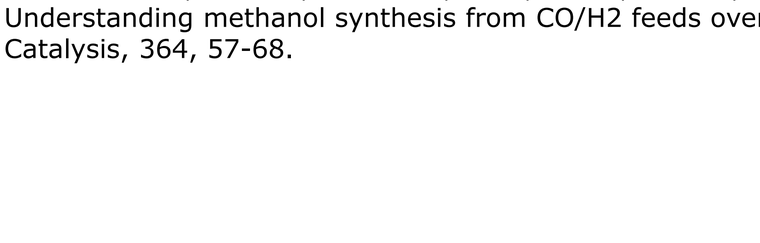






Oxygen vacancy control

% Ce^{3+} calculated from powder XRD lattice parameters
Using 1000°C dry air calcination as 100% Ce^{4+}
As synthesised sample;
300-500°C calcination in dry air;
Reduction <u>after</u> 400°C DA calcination:
Wet: Vitamin C + $NaBH_4$
Gas: 450-550°C H_2



Au/CeO_2 characterisation

Homogeneously dispersed Au nanoparticles with approx. 2nm diameter deposited on CeO_2 surface

Catalytic performance

Synthesised catalyst reduces CO_2 upon illumination
A good activity coupled with a strong selectivity towards CO

Conclusions

- → Flexible, reproducible CeO_2 synthesis method: spherical shape, no organic residual and fluorite crystal structure.
- → Oxygen vacancy content quantified using powder XRD, will be verified using XPS
- → Au deposited homogeneously on CeO_2 support
- → Good activity of catalyst and high selectivity for CO
- → **Foundation has been made to investigate underlying mechanisms in the 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.

[3]van de Water, L. G. A., Wilkinson, S. K., Smith, R. A. P., & Watson, M. J. (2018). Understanding methanol synthesis from CO/H2 feeds over Cu/CeO2 catalysts. Journal of Catalysis, 364, 57-68.

Acknowledgements

Interreg
EUROPESE UNIE
Vlaanderen-Nederland
Europees Fonds voor Regionale Ontwikkeling
IMO-IMOMEC
UHASSELT
imec
project LUMEN
sunlight fueled chemistry
Energy Ville