

The role of temperature in plasmonic photocatalysis: large scale modelling and 3D thermal imaging

Adarsh B Vasista¹, Jaime Ortega Arroyo¹, Daria Burova^{3,4,5}, Jonathan van den Ham², Nicole Meulendijks², Ken Elen^{3,4,5}, An Hardy^{3,4,5}, Marlies K. Van Bael^{3,4,5}, Pascal Buskens^{2,3} and Romain Quidant¹

¹Nanophotonic Systems Laboratory, Eidgenössische Technische Hochschule (ETH) Zürich, Switzerland

²The Netherlands Organisation for Applied Scientific Research (TNO), Eindhoven, The Netherlands

³Design and Synthesis of Inorganic Materials (DESINE), Institute for Materials Research, Hasselt University, Diepenbeek, Belgium

⁴Imec Vzw, Imomec Associated Laboratory, Diepenbeek, Belgium

⁵EnergyVille, Genk, Belgium

E-mail: avasista@ethz.ch

Due to the rapid pace of climate change, it is imperative to find cost-effective and scalable approaches to produce clean energy and to reduce the carbon footprint. In this context, solar-powered production of methane through the conversion of CO₂ and H₂ (Sabatier process) is a promising option [1]. In such a process, the conversion yield can be greatly increased with plasmonic catalysts, by exploiting their ability to efficiently convert light into heat. However, the complex geometry of the catalyst in the form of plasmonic NPs, and the large physical size of the experiment (Figure 1 a), poses a serious challenge for accurately modelling and measuring the photothermal contribution towards the catalytic process.

From a simulation perspective, the prohibitively huge demand of computational resources from commercial solvers significantly limits the modelling of photothermal conversion in catalysis. To circumvent this issue, we developed a 3D Green's function method coupled with the discrete dipole approximation (DDA) that calculates large-scale 3D thermal profiles resulting from photothermal conversion. Using the said approach, we studied the collective thermal effects in the catalyst bed, and unraveled the critical relationship between the temperature, and the sizes of the catalyst NPs and the host, respectively (Figure 1b-c).

From an experimental perspective, the non-propagative nature of heat makes measuring 3D thermal profiles in complex nanoparticle ensembles like catalysts challenging. Using optical diffraction tomography (ODT) and exploiting the variation of the media refractive index with temperature, we retrieved the 3D temperature profile of the catalyst ensemble under illumination (Figure 1d) [2,3]. By monitoring the temperature dynamics inside we characterized the temperature evolution as a function of the concentration and material properties of the catalyst. Finally, we compared the yield of methane production under similar catalytic conditions to quantify photothermal and non-thermal contributions towards the Sabatier process.

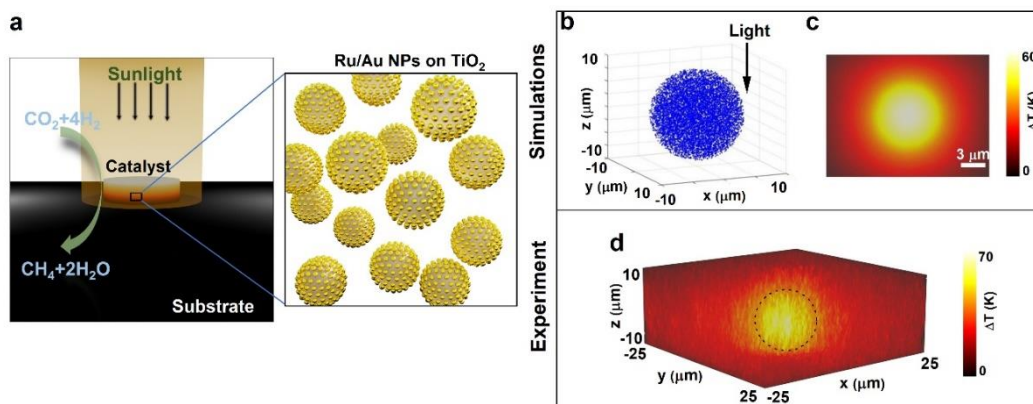


Fig. 1 (a) Schematic of the experiment (b,c) Spatial coordinates of the Ru/TiO₂ NPs distributed inside a sphere of radius 7.5 μm with the corresponding thermal profile calculated using 3D green's dyadic method. (d) Experimentally measured thermal maps for a Ru/TiO₂ catalytic ensemble using ODT. The dashed circle represents the spot size of the illumination.

We believe that our results on 3D thermal mapping of the catalyst ensembles together with the large-scale modelling provide important insights into the photo-thermal effects in catalysis. We anticipate these results will stimulate further experimental and theoretical studies to quantify the photothermal vis-à-vis non-thermal contributions towards photocatalysis.

References

- [1] (a) Grote R, Habets R, Rohlfis J, Sastre F, Meulendijks N, Xu M, Verheijen MA, Elen K, Hardy A, Van Bael MK, Den Hartog T, Buskens P, *ChemCatChem* 12, 5618 (2020); (b) Zhao T, Yang Z, Tang Y, Liu J, Wang F, *Energy Fuels* 36, 6711 (2022).
- [2] Oh J, Lee G, Rho J, Shin S, Lee B J, Nam Y, Park Y K, *Phys. Rev. Applied*. 11, 044079 (2019)
- [3] Vasista A B, Ciraulo B, Arroyo J A, Quidant R, *manuscript under preparation*, (2023)