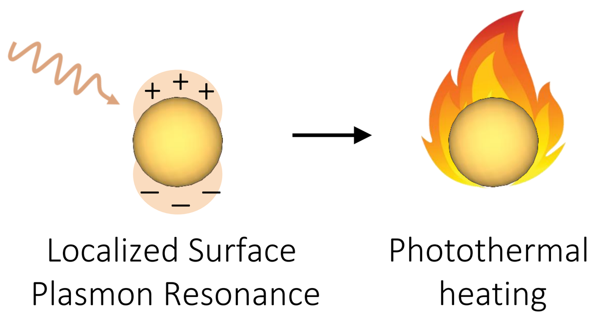
A Nanoscale Plasmonic Reactor: Light-Driven Synthesis of Individual Core@Shell Nanoparticles

Rifat Kamarudheen,[1,2] Gayatri Kumari,[1,2] Andrea Baldi [1,2,3]

[1]DIFFER - Dutch Institute for Fundamental Energy Research, 5612 AJ Eindhoven, The Netherlands
[2]Institute for Complex Molecular Systems, Eindhoven University of Technology, 5600 MB Eindhoven, The Netherlands
[3]Department of Physics and Astronomy, Vrije Universiteit Amsterdam, 1081 HV Amsterdam, The Netherlands

DIFFER
Dutch Institute for Fundamental Energy Research

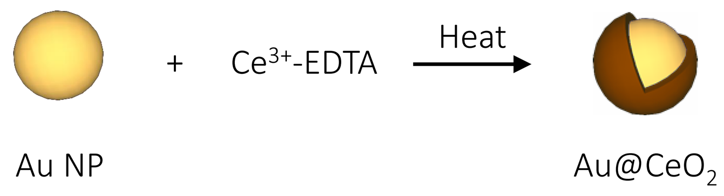
1. Motivation: Non-radiative decay of plasmons can drive chemistry



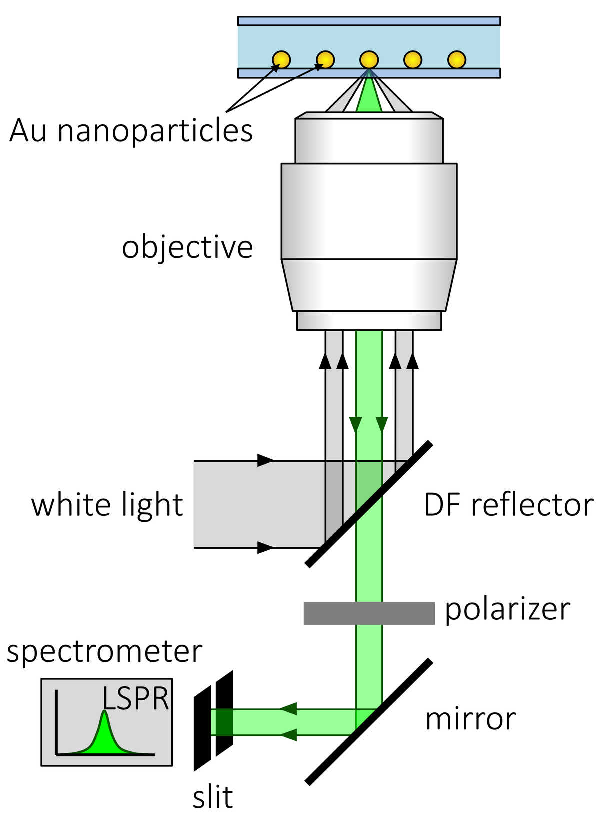
Nanostructures made of noble metals such as Au, Ag and Cu support localized surface plasmon resonances (LSPRs), which are collective oscillations of their free electrons, driven by light.[1] These surface plasmons decay by locally heating the nanoparticles, which can drive chemical reactions.[2]

Here, we demonstrate how **localized photothermal effects** can be used to produce spatially-confined **nanoreactors** by **activating, controlling, and spectroscopically** following the **growth** of individual metal@semiconductor **core@shell nanoparticles**.

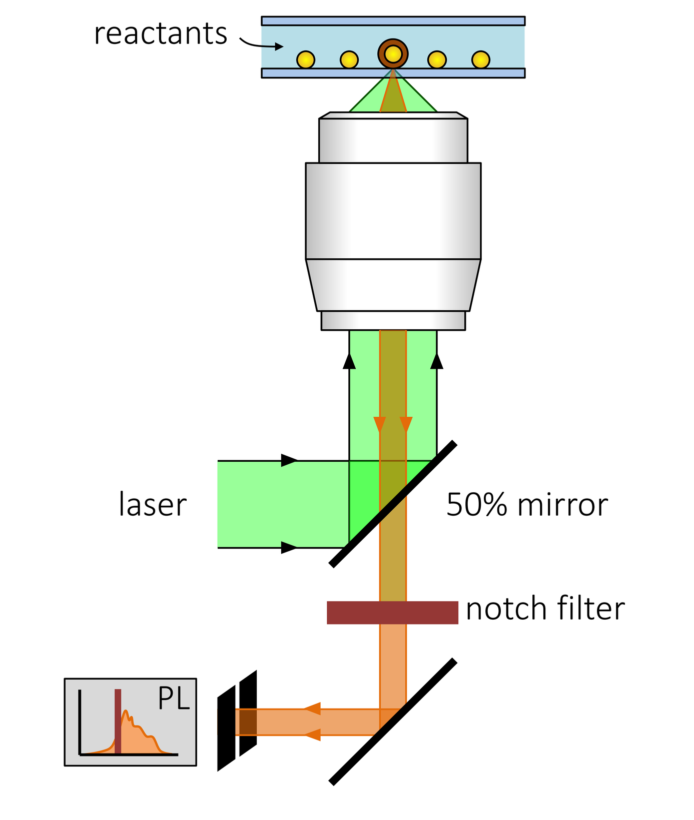
2. Demonstrating the photothermal activation and nanoscale control of chemical reactions, using a core@shell synthesis



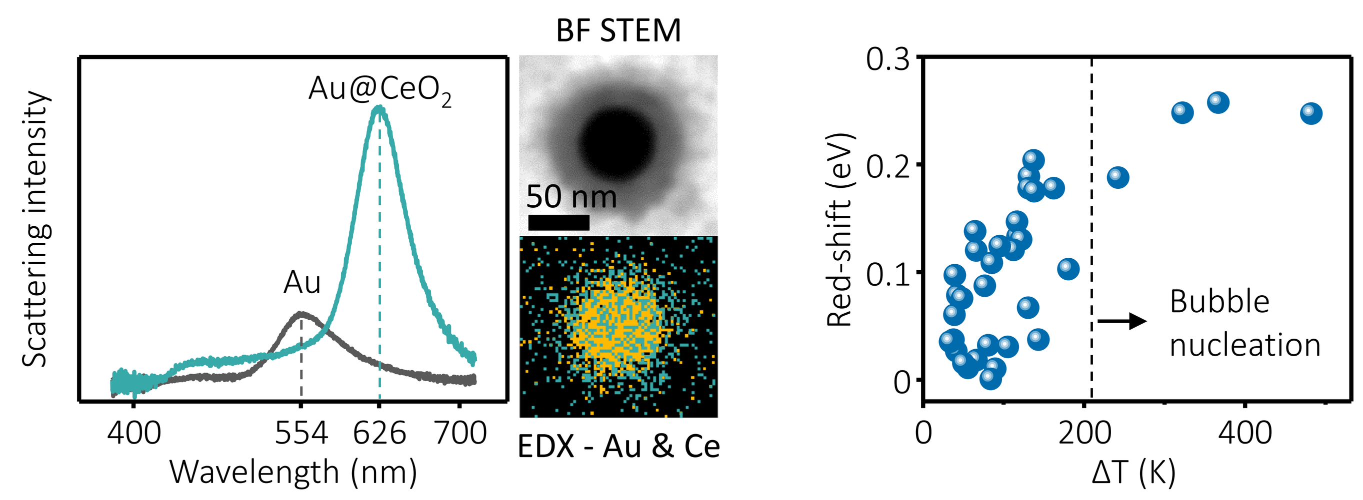
This temperature-activated $Au@CeO_2$ core@shell nanoparticle (NP) synthesis occurs at higher temperatures such as 90 °C in ensemble conditions.[3] We perform this synthesis under photothermal heating of 'individual' Au NPs.



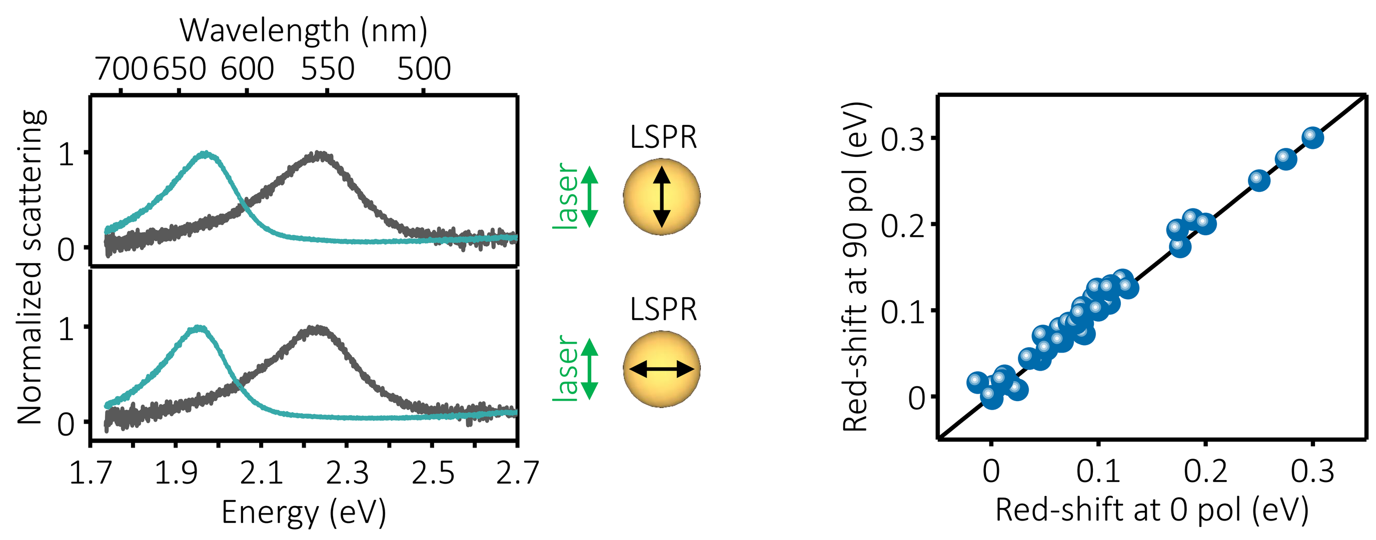
Dark-field single-particle scattering spectroscopy



Single-particle irradiation & *In situ* photoluminescence spectroscopy

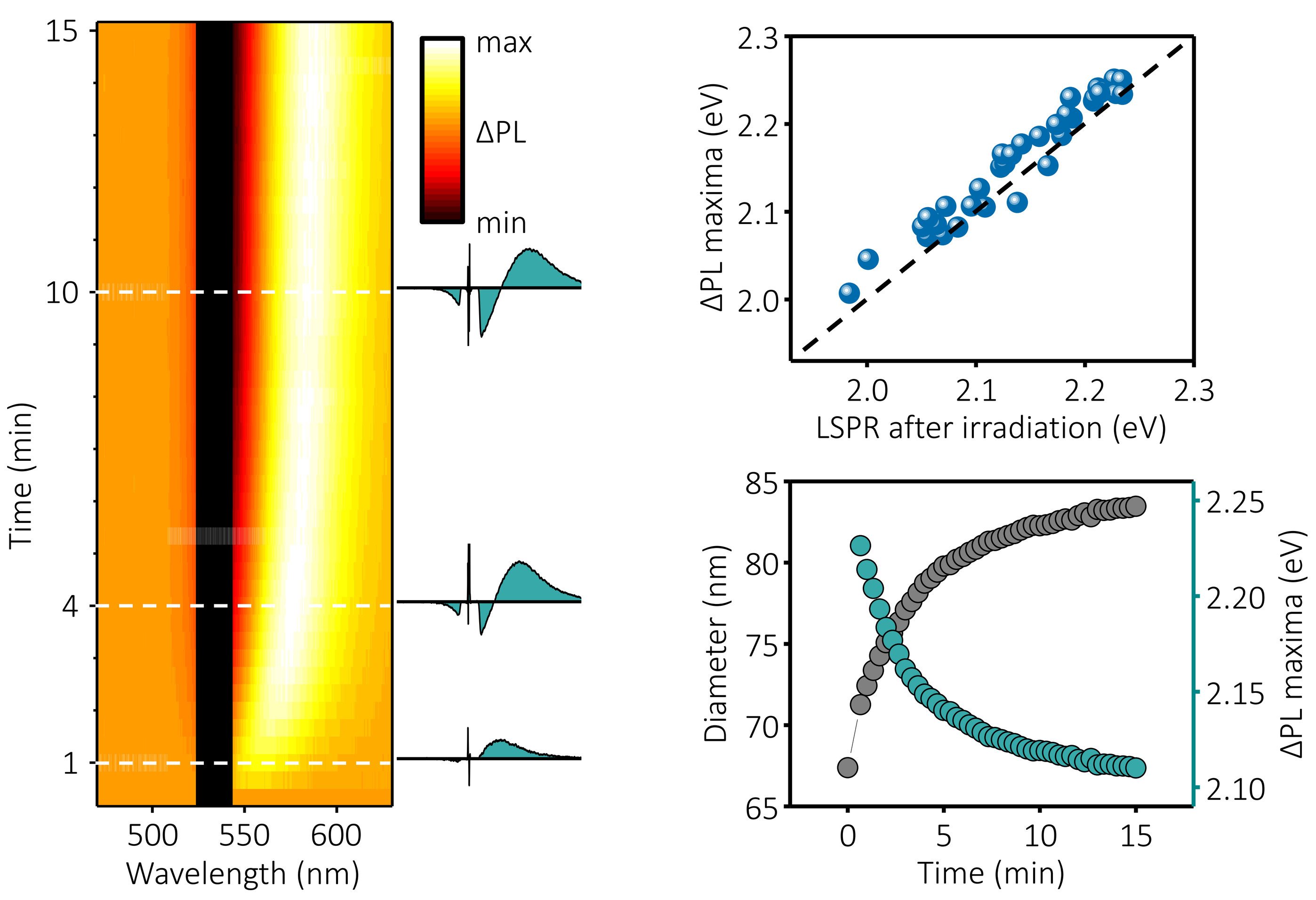


Under irradiation, we observe a red-shift in the LSPR of Au NP due to the growth of CeO_2 shell. Electron microscopy and EDX maps confirm the formation of $Au@CeO_2$ core@shell NPs. The photothermal shell growth scales with the nanoparticle temperature.



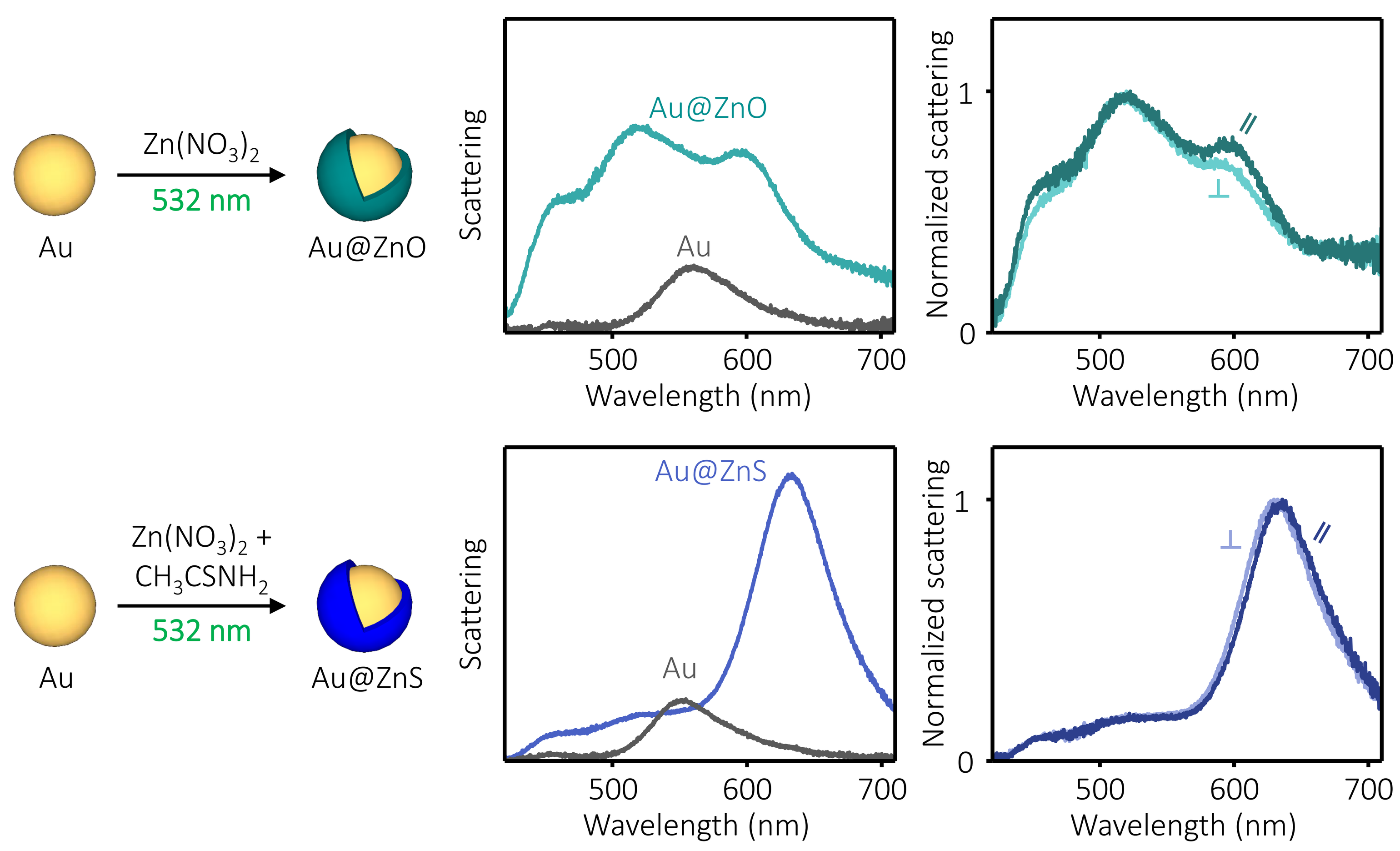
Photothermally-grown ceria shell is isotropic in nature, as confirmed by polarization-dependent scattering spectra on several individual NPs.

3. *In situ* tracking of the photothermal growth of nanoparticles

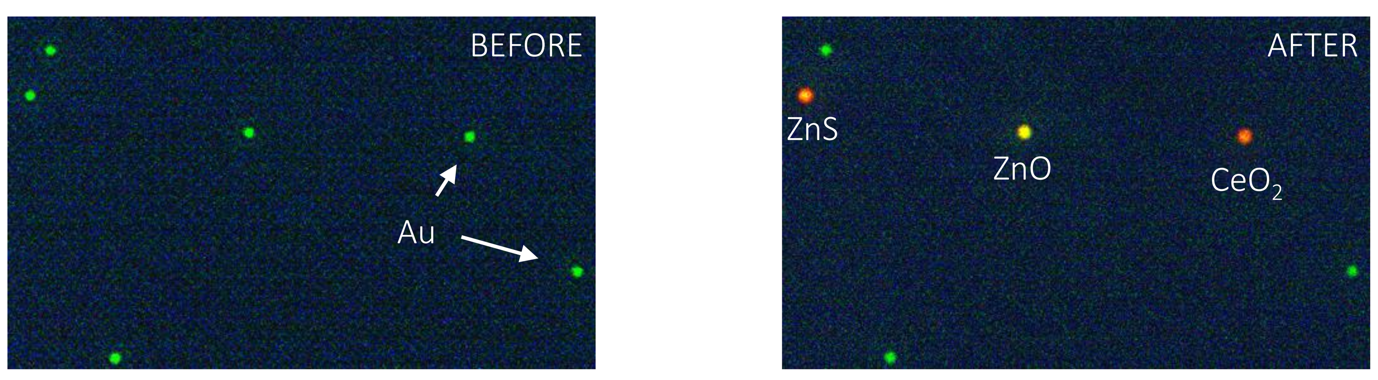


Real-time tracking of the photoluminescence of the growing core@shell nanoparticle is useful to study their growth kinetics.

4. Versatility of the technique and substrate patterning



We demonstrate the growth of metal oxides and metal sulfides using photothermal nanoreactors.



5. Conclusion & Outlook

- Localized temperature gradients produced by plasmonic heating can be exploited to drive spatially confined chemical reactions.
- Combining our technique with automated particle centering algorithms, one can envisage fast printing of hierarchical nanoparticles with advanced functionalities over large areas.

References

[1] Brongersma, M. L., Halas, N. J. & Nordlander, P. *Nat. Nanotechnol.* **10**, 25–34 (2015).
[2] Baffou, G. & Quidant, R. *Chem. Soc. Rev.* **43**, 3898–3907 (2014).
[3] Li, B. *et al. ACS Nano* **8**, 8152–8162 (2014).

Acknowledgements

- This work is partially supported by the FOM/NWO program "Photosynthesis of nanomaterials: developing nanostructured photocatalysts for solar fuel generation using light".
- We are also grateful to Guillaume Baffou (Institut Fresnel) for all the helpful discussions.