Andrew Fellowship Completion Report – Dr Simon Freakley, University of Bath

Accelerating Catalytic Reactions Using Visible Light

Background

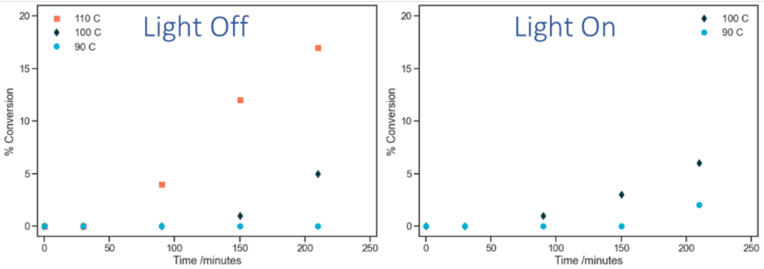
This fellowship focused on the development of catalytic materials capable of harnessing visible light through the surface plasmon resonance (SPR) of copper (Cu), silver (Ag), and gold (Au) nanoparticles. SPR enabled the direct transfer of energy into catalytic nanostructures by inducing collective oscillations of the conduction electrons at the nanoparticle surface. As Cu, Ag, and Au exhibited SPR in the visible light spectrum, they were identified as promising candidates for light-driven catalysis. The precise mechanism by which SPR facilitates chemical transformations remains under active investigation. Proposed mechanisms included localised heating via plasmon–phonon coupling and the generation of energetic "hot" electrons capable of activating chemical bonds at the nanoparticle surface. Initial research efforts focused on Cu-based catalysts to promote liquid-phase hydrogenation and dehydrogenation reactions under mild conditions. The aim was to reduce or replace the use of precious metals such as palladium (Pd) and platinum (Pt). A key objective was to establish structure–activity relationships governing both light-enhanced and thermally driven catalytic performance.

Progress During the Fellowship – Key Results

During the initial six months of the fellowship, efforts were dedicated to designing and constructing a reactor system capable of performing catalytic reactions under conditions closely resembling standard heterogeneous catalysis. This involved sourcing and evaluating a windowed autoclave reactor, which was selected for its ability to replicate low-pressure catalytic testing environments. The chosen reactor features a borosilicate glass window integrated into the top of the vessel (see image below), allowing for controlled light exposure during reactions. It is rated for operation up to 8 bar and 200 °C, making it suitable for investigating low-pressure hydrogenation and dehydrogenation processes. Illumination is provided by a xenon (Xe) arc lamp, with filters applied to remove ultraviolet (UV, <420 nm) and infrared (IR) wavelengths. This ensures that only visible light contributes to the reaction, enabling precise evaluation of light-driven catalytic effects.

Dehydrogenation Catalysis

Acceptorless dehydrogenation is a chemical reaction in which hydrogen atoms are removed from a molecule without the involvement of an external hydrogen acceptor. This process typically results in the formation of unsaturated compounds and the release of hydrogen gas as a by-product. It is commonly used in organic synthesis and catalysis to create double bonds or aromatic systems, enhancing the efficiency of hydrogen production and molecular transformations, commonly employing a Pd catalyst. Initial efforts to work with metallic copper (Cu) catalysts encountered challenges due to rapid oxidation, which led to the formation of copper oxide passivated materials.



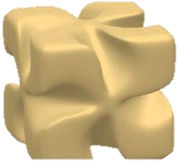
Following this a new synthesis method was devised based on colloidal Cu particles preparation and immobilisation which resulted in significantly increased reproducibility. SEM-EDX analysis indicated Cu particle sizes in the range of 30–50 nm with a thin layer Cu-oxide surface. UV/Vis spectroscopy revealed an absorption peak at 565 nm, characteristic of plasmonic nanoparticles and comparable to colloidal gold, with the materials exhibiting a similar purple hue when freshly reduced. A key observation was that under reaction conditions the colour of the samples changed from light green indicating oxidised Cu to deep purple indicating reduced copper suggesting an induction period where the catalyst is undergoing a change – this correlates well with the onset of product formation. We were able to significantly reduce this induction period by illuminating the catalysts with light by 90 mins therefore switching on the materials by accelerating Cu oxide reduction with illumination. In acceptorless dehydrogenation reactions using 1-phenylethanol as a model substrate, illumination of the catalyst enhanced the reaction rate by a factor of 2.5 (0.0019 min^{-1} vs. 0.0049 min^{-1}), with only a minimal induction period and reduced the activation energy by over 50%. These results suggest that light can be used as an effective means to not only activate Cu catalysts by accelerating surface reduction but also increase the reactions rate of this important class of reactions.

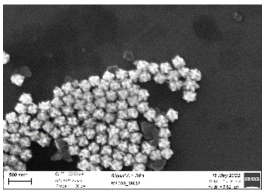
Transfer Hydrogenation using Au Catalysts

Transfer hydrogenation is a catalytic process that involves the transfer of hydrogen from a donor molecule to an acceptor without the use of molecular hydrogen. Gold catalysts, particularly in the form of nanoparticles supported on various substrates, have shown promising activity in this reaction. Gold catalysts exhibit excellent selectivity and stability, making them suitable for various organic transformations unlike Pd or Pt catalysts which are very active but can have limited selectivity when multiple functional groups are present. I explored the role of Au's surface plasmon resonance in transfer hydrogenation reactions and found that illuminating Au particles with visible light (~10 nm) resulted in a reduction in the reactions apparent activation energy from 106 to 48 kJ mol^{-1}, significantly accelerating the reaction at mild conditions. It was observed that the plasmonic enhancement was also dependent on temperature and work is underway to develop models to i) determine how the key elementary steps are affected by light absorption in collaboration with DFT expertise and ii) to develop a kinetic approach to understanding how to disentangle thermal and photo effects in these systems.

Catalysis Using Helicoid Particles – Collaboration with Kings College London

Helicoid nanoparticles are a novel class of nanomaterials characterised by their helical or spiral structures. These unique shapes impart distinctive optical, mechanical, and chemical properties, making them valuable in various applications. The helicoid geometry enhances light absorption, scattering, and chiral interactions, making them useful in photonic devices, sensors, and catalysis. Additionally, they have tuneable surface properties, allowing them to form surface alloys on top of the chiral cores. Working with Kings College, we aimed to synthesise helical Au colloidal particles in IPA with minimal surfactants present. This was successful in producing approximately 190 nm chiral Au particles. These particles interact with right-hand and left-hand polarised light differently, as electric fields are concentrated onto different parts of the particles, as simulated below. We have successfully deposited Pd onto these particles to act as a catalyst surface. Recently, we conducted the first tests of the AuPd surfaces for the transfer hydrogenation reaction (as above) and observed for the first time that the particle's photocatalytic activity depends on the chirality of the light and the chirality of the surface.





There was a 1.8x rate enhancement when the chirality of the light matched the chirality of the particles. Further work is ongoing to study if this has any effect on the chirality of the products formed.

Grant Funding

During the initial phase of the fellowship, I began to build networks both within my university and across the UK. Following a joint symposium which I was invited to speak at between the UK Catalysis Hub and researchers in an EPSRC Programme Grant "Reactive Plasmonics" I was actively involved in a grant application to develop the Programme Grant "Catalytic Plasmonics". *This was announced as successful with a £10m investment from the EPSRC (https://www.csct.ac.uk/freakley-light-driven-energy-conversion-grant/).* The grant incorporates many themes of this fellowship and gives me a greater opportunity to accelerate progress over the coming years. Since the award of the EPSRC Programme Grant "Catalytic Plasmonics", I have networked extensively with the partners in the UK Catalysis Hub (Hardacre, Hutchings, Catlow and Beale), Kings College London (Dickson, Zayats) and Imperial College (Meier and Stephens) to develop projects and I am leading the work package on energy applications. Over the course of the fellowship, I have attended and spoken at many international and national meetings such as the UKCC, EuropaCat and ICC. In addition, I have co-organised an RSC meeting on Chemical Feedstocks for the Sustainable industry. In addition, I have led a team to devise an outreach exhibit which was selected for the Royal Society Summer Science Exhibition in July'25 which has themes closely aligned with the fellowship.

Conclusions

This fellowship has been instrumental in advancing both my scientific expertise and professional development. Through the design and implementation of a bespoke light-driven catalytic reactor system, I gained valuable experience in experimental setup and design. My work on copper-based catalysts led to the development of reproducible synthesis methods and revealed the potential of visible light to activate and enhance catalytic performance, particularly in dehydrogenation reactions. This has led to 3 planned publications which are being finalised with collaborators. Collaborations with institutions such as King's College London enabled me to explore cutting-edge materials like helicoid nanoparticles, uncovering novel light–chirality interactions in catalysis. These interdisciplinary efforts broadened my research scope and introduced new dimensions to catalyst design. The fellowship also served as a springboard for significant grant success, including my leadership role in the £10 million EPSRC Programme Grant "Catalytic Plasmonics." This has positioned me at the forefront of a national research network and provided a platform to lead a major work package on energy applications. Additionally, my involvement in national and international conferences, outreach initiatives, and academic symposia has strengthened my communication skills and expanded my professional network. Overall, the fellowship has not only deepened my understanding of plasmonic catalysis but also established a strong foundation for future leadership in sustainable catalysis research.