Cleaning the **future**

Dr Robert Palgrave has been working on a variety of new photocatalysts, with the goal of reducing water and air pollution and finding new sources of clean energy

Could you begin by outlining the aims of the research project 'Discovery of New Multi-phase Photocatalysts' and explain why the project was established?

One of the biggest challenges of our era is securing the future of our energy supply. Fossil fuels are a finite resource; one day they will run out. Before that, they will likely do irreparable damage to our atmosphere if we continue using them. We need to find an alternative source. Luckily, the Sun provides far more energy to the Earth in a single day than the whole of humanity uses in a year. The challenge is to harness this energy. One way is through photovoltaic (PV) materials, like silicon solar cells, which turn sunlight into electricity. Another way – which I am investigating with this project – is to capture sunlight as chemical fuels, like hydrogen or methanol. By storing energy as fuels, it can be released as needed; for example, powering a fuel cell car.

This project is primarily aimed at creating new materials that can harness sunlight and store it as chemical fuel. These materials are called photocatalysts, and they use photons to drive chemical reactions, like water splitting or the chemical reduction of carbon dioxide. Of course, the natural world is full of materials that do just that; for example, green plants use photosynthesis to store the energy from sunlight as carbohydrate molecules. In this project, I have taken inspiration from the mechanism of natural photosynthesis to try to build artificial photocatalysts that are more efficient.

What initially attracted you to chemistry?

Like many people, I was inspired by my teachers at school and as an undergraduate, and by mentors at the different universities in which I've researched. At every stage, I've felt inspired to go further in the subject. With chemistry there is always something new to discover; after all, we have the whole periodic table to play with. My supervisor at the University of Oxford had a periodic table in his office and crossed off an element each time he had published a piece of research on it. He finally crossed them all off (at least the non-radioactive ones!) just before retiring. With chemistry there's plenty to keep you going for a whole lifetime of research.

The project is now in its final year. What are the greatest challenges you have faced so far, and how have you overcome them?

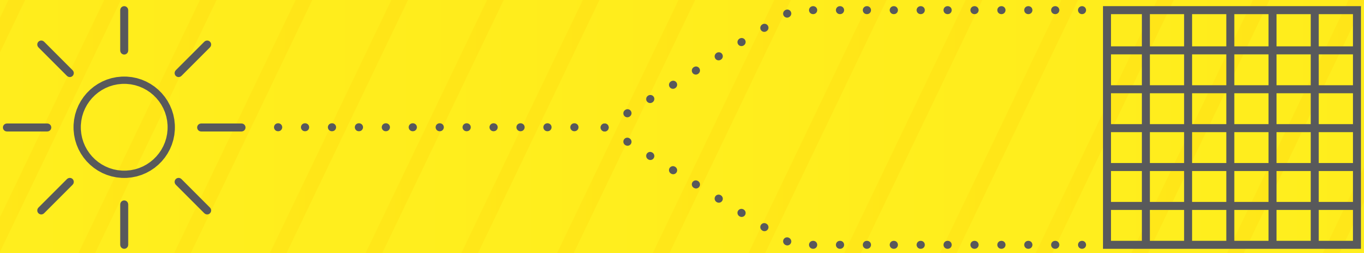
It has proven very challenging to measure the photocatalysis of our epitaxial film samples. Traditionally, photocatalysts are produced as powders with a high surface area – this means there are many surface reaction sites for producing hydrogen gas, for example. However, thin films have much lower surface areas, so the amount of hydrogen produced is too small to detect. To get around this, we need to develop new ways to measure the photocatalytic rate to give us a reliable approximation to the hydrogen production rate. This has been difficult, but we are moving towards a reliable 'surrogate reaction' we hope will be useful to others working in this field as well, as it is much quicker and easier than measuring the hydrogen production directly.

In light of the UK Government's policy to increase the use of low-carbon technologies, how will your research help the country meet its climate change targets? What do your findings mean for Europe's energy consumption?

The UK Government is committed to achieving 15 per cent of its energy from renewable sources by 2020. To meet this aim, a variety of methods will be required, with solar energy capture likely to be a major component. I hope this project will help fundamental research into new solar energy materials, which might form part of the solution to this global problem.

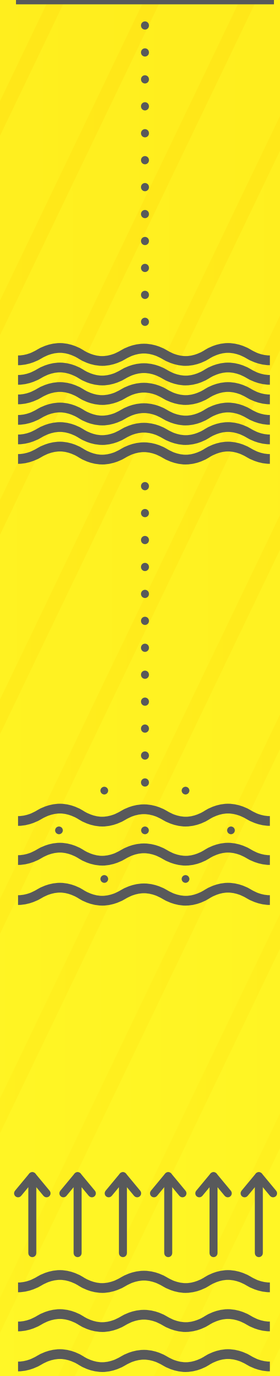
Could you expand on any plans you might have for future projects? Are you involved in any other areas of research?

I'm interested in all kinds of energy materials, photovoltaics, photocatalysts and energy efficient materials. I have ongoing projects working towards developing new solar cell materials, which is currently an active area of research with major breakthroughs being made by UK-based scientists. I'm also working on energy efficient window coatings with colleagues in Singapore.



Tap into **the sun**

Ongoing research at **University College London** is redefining the field of photocatalysis, creating improved methods to study photocatalyst function. They are also considering Z-scheme catalysts with the hope of creating visible-light activated photocatalysts



THE DEVELOPMENT AND application of photocatalysts represent a booming industry, predicted to reach a value of US $1.7 billion this year. Photocatalysts speed up chemical reactions and are driven by the absorption of light, allowing otherwise slow reactions to take place at rates relevant for application in a variety of fields. Their applications are already vast, from self-cleaning windows, fabrics and pavements to purifying drinking water. They can also be used to remove pollutants within the atmosphere.

Despite their increasing prominence in everyday life, photocatalysts have a range of yet unfulfilled applications, owing partly to their inability to utilise the visible spectrum of light. Dr Robert Palgrave of University College London (UCL) is examining the limitations of photocatalysts, and the primary aim of his work is to develop ones that are not restricted to UV light. He is also seeking to elucidate the basic science underlying their function, envisioning that his work will one day lead to an increase in their efficiency. To meet these goals, Palgrave is focusing his research on two areas: the use of epitaxial thin films and biomimetic Z-scheme systems.

EPITAXIAL THIN FILMS

In order to develop efficient photocatalysts, scientists need to study these materials at the nanoscale. Specifically, there is a need to better understand the nanoscale properties that contribute to their catalytic behaviour. Although this is an active field of research, it is held at bay to some extent due to the complexity of nanomaterial samples, such as nanopowders. Nanopowders exhibit variable properties such as phase composition and surface morphology that are difficult to characterise or control. These undefined properties can affect the behaviour of the material, leading to an inherent uncertainty when trying to design new photocatalysts. Consequently, it is difficult to relate a given nanomaterial's properties to its overall function.

Palgrave is developing alternative model samples for use in photocatalyst studies – epitaxial thin films. The film consists of a layer of atoms of a given material, adsorbed in an ordered orientation onto the surface of a crystalline substrate with a known structure. His method is novel and allows for the production of nanosamples of well-defined structure and composition, which is essential for studies that relate the function of a given nanomaterial to its underlying structure. Palgrave's epitaxial thin films will also improve future researchers' understanding of the underlying properties of photocatalysts, enabling scientists in the field to create catalysts that are more efficient. Alongside the development of these new samples, Palgrave is developing new methods for specifically studying the photocatalysis of epitaxial films.

BIOMIMETIC Z-SCHEMES

Most photocatalysts are restricted to only using UV light, limiting their widespread use. Catalysts that rely on visible light can be more useful than those requiring UV radiation and the emergence of such technology will open new avenues for the development of photocatalyst applications, as well as improve upon existing technologies. Currently, photocatalysts generally consist of only one catatlytic material, which absorbs light and facilitates a combination of oxidation and reduction (redox) reactions. "When we use a single photocatalyst material, it must absorb the

INTELLIGENCE

DISCOVERY OF NEW MULTI-PHASE PHOTOCATALYSTS

OBJECTIVES

- To use solid-state and materials chemistry to discover new energy materials, including photocatalysts and photovoltaic materials
- To synthesise materials as thin films, ceramics and nanoparticles and carry out studies on both fundamental properties and practical applications

KEY COLLABORATORS

Professor Russ Egdell; **Professor Richard Compton**, University of Oxford, UK

Dr David Scanlon, University College London (UCL), UK

Dr David Payne; **Dr Shelly Moram**, Imperial College London, UK

Professor Ken Durose, University of Liverpool, UK

Professor Aron Walsh, University of Bath, UK

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ROBERT PALGRAVE completed his PhD in Chemistry at UCL in 2007, under the supervision of Professor Ivan Parkin. Subsequently, he did postdoctoral research at the University of Oxford with Professor Russ Egdell and at the University of Liverpool with Professor Matt Rosseinsky, before returning to UCL with an appointment as Lecturer in Inorganic and Materials Chemistry in 2012.

light and carry out both oxidation and reduction. It is very challenging to design a single material that can do all that. Despite over two decades of research worldwide, no single material has been found that is sufficiently active in visible light," states Palgrave, who is working to design new materials that could solve this problem.

> Dr Robert Palgrave of University College London focuses on the limitations of photocatalysts, seeking to elucidate the basic science underlying their function

To do so, Palgrave has turned his attention to the natural world. The most abundant and well-known photocatalytic reaction occurs in plants, and this reaction, known as photosynthesis, is driven by visible-range light. Photosynthesis allows energy from visible light to be converted into chemical energy in a set of redox reactions. This elegant and efficient process is possible in plants because they have not one catalyst, but two – photosystem-I and -II. They are coupled by a redox mediator in an arrangement that has come to be known as a Z-scheme. This scheme overcomes the energy threshold of reactions by separating the reduction and the oxidation reaction's roles. Palgrave explains: "Instead of using one high-energy ultraviolet photon, a Z-scheme uses two lower energy visible photons for the same reaction".

Palgrave hopes to draw ideas from this system, applying the basic principle utilised by plants to artificial systems of photocatalytic processes; however, instead of using the naturally occurring photosystem-I and -II, Palgrave's work considers the coupling of two solid-state artificial photocatalytic materials that are connected by a heterojunction. To make his approach work, Palgrave is studying these complex Z-schemes using his epitaxial films to elucidate their underlying mechanisms and to find out how to make them more efficient.

TESTING Z-SCHEMES

One of the methods Palgrave is using to understand Z-schemes is photoemission spectroscopy, which allows him to assess the energy level offset of two different materials. This is important for Z-schemes because they require two catalysts with carefully aligned energy levels to be coupled. He has tested this method on rutile and anatase, two forms of the well-known catalyst TiO_2. Palgrave and his collaborators, computational chemists Professor Aron Walsh and Dr David Scanlon of the University of Bath and UCL, respectively, have demonstrated why rutile-anatase mixtures are better photocatalysts than either rutile or anatase individually. Future work seeks to apply this to novel Z-scheme materials.

PHOTOCATALYSTIC APPLICATIONS

With new tools to characterise and study photocatalysts, Palgrave predicts the future will see novel applications and increased catalytic efficiency. Visible light photocatalysts have a wide range of applications that UV catalysts do not. For example, they could be used in the development of antimicrobial coatings, which self-sanitise, killing any microbes on the surface. This has obvious practical applications in healthcare, where UV radiation is required to at present activate self-cleaning properties of medical equipment.

But the biggest potential application is in clean energy production. Photocatalysts can split water into its constituent elements; when activated with sunlight, this process stores the energy from the sun as the chemical fuel hydrogen. Due to their increased efficiency under visible light, photocatalysts may become an essential part of the solution to society's current energy problems. The economic consequences are significant. Palgrave explains: "Photocatalysts may have a transformative impact on the energy economy, enabling the necessary shift away from fossil fuel towards renewable sources".