Impact Objectives

- Investigate the physics and chemistry of kesterite solar cells fabricated from nanoparticle inks
- Improve our understanding of the solar cell interfaces, stacked-layer microstructure and electronic properties when chemical impurities are added to the fabrication process
- Investigate photonic curing as an alternative to high-thermal budget heating for speeding manufacturing processes

Photovoltaic paint

***Dr Guillaume Zoppi** and **Dr Neil Beattie** are focused on creating cost-efficient thin film photovoltaics that may revolutionise the renewables industry and help countries move away from a reliance on fossil fuels*

Dr Guillaume Zoppi

Dr Neil Beattie

What are photovoltaic nanoparticle inks and what is their significance?

GZ: Nanoparticle inks are solutions that contain small crystals of between 10 and 20nm in size. These tiny crystals or nanoparticles are stable in solutions and are not volatile when dried, thereby making them safe to handle. By layering dispersible nanoparticles as inks or paints, our vision is to develop these, so they can be spread onto any surface to generate electricity on exposure to sunlight. These can be used in many more applications than the glass and silicon-based panels fixed on rooftops. For instance, we envisage our paints being incorporated into building design and other fixed structures to greatly improve energy efficiency. In addition, our aim is to make these inks suitable for flexible substrates for creating and powering wearable technologies and the Internet of Things. Along with the rest of the world, the UK needs to continue to move away from the use of fossil fuels for its energy needs, both to tackle climate change and to save costs. Solar power offers one of the best opportunity for this.

What have the main challenges been in terms of achieving your research goals so far?

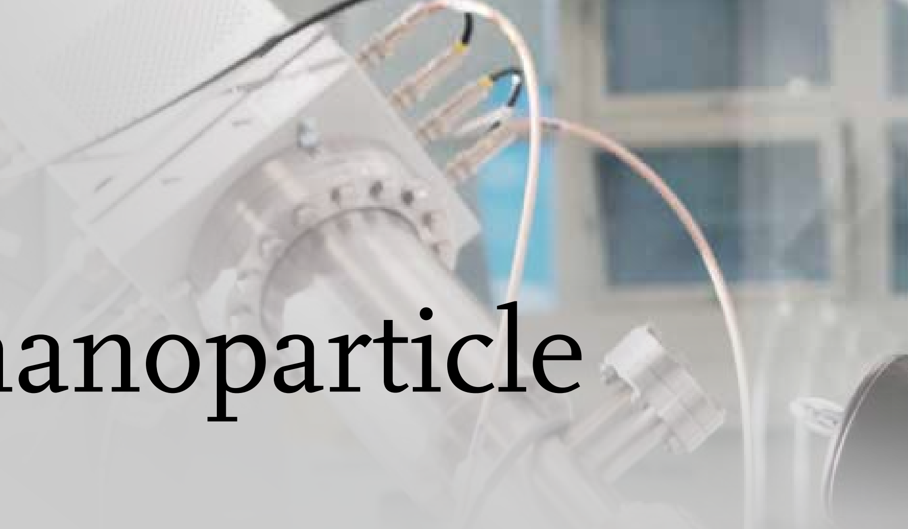
GZ: Time has been one of the main challenges on this project. The present Engineering and Physical Sciences Council (EPSCR) First Grant Scheme award is for just two years and has allowed us to take on a research fellow to work on the project for one year and deliver the set of ambitious objectives. In our case, the research fellow was the student who developed the fabrication process during our first Royal Society-funded project, so we were quickly off the ground and able to achieve many of the original targets. Also, producing efficient photovoltaic (PV) devices is very challenging as the device structure includes seven layers and 15 or more steps and processes, all of which have to be carefully monitored to avoid mistakes. However, this puts us in a unique position as one of the few laboratories in the UK able to routinely complete thin film PV devices.

NB: The technical challenges have been many and varied. Our chemical-based method of mixing the required elements is relatively inexpensive and resilient to process evolution. However, the main disadvantage of this technique is that in their as-grown form, the nanocrystals are not very efficient as solar absorbers when completed into solar devices, despite being very good at absorbing photons. The primary reason for this is the presence of a dense network of grain boundaries that cause the photon-generated carriers to recombine and not contribute to the output current.

What is your background and how has that led you to your current line of investigation?

NB: In 2009, I decided to combine my industrial experience and knowledge of semiconductor nanotechnology to work on solar energy research and so joined Northumbria University as a senior lecturer in physics and electrical engineering. With Dr Zoppi, we were able to win a prestigious Royal Society research grant to fabricate sustainable solar paint, which was the precursor to this project.

GZ: I have been involved in inorganic thin film photovoltaics since starting my PhD back in 2002. Since then, I have been involved in investigating many different compounds, all of which have included at least one of the following elements: telluride, sulphur and selenium. Over a decade ago, I came across the semiconductor CZTSSe, which contains copper, zinc, tin, sulphur and selenium ($Cu_2ZnSn(S,Se)_4$). This was attractive as each of the constituents is naturally abundant compared to materials containing indium and gallium. This compound is the subject of our current project. ▶

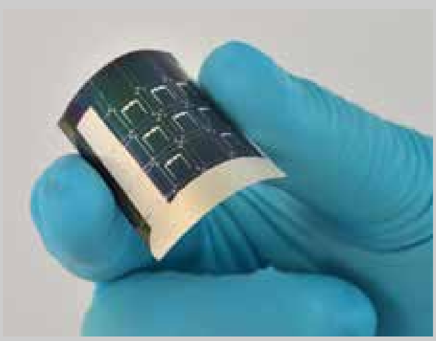


Thin film nanoparticle solar cells

Northumbria University *in the UK is a pioneer in photovoltaics research and is part of the* ***North East Centre for Energy Materials****. Together, they are developing solar cells using nanoparticle inks made from readily-available, non-toxic elements*

Associate Professors Dr Guillaume Zoppi and Dr Neil Beattie from Northumbria University are close to realising their ambition to create flexible, spreadable thin film solar cells from nanoparticle inks. Principal Investigator Zoppi tells us that close to a quarter of the UK's electricity was generated by solar photovoltaics during a favourable day in May 2017 and that: 'There is a growing interest nationally and internationally to find alternatives to silicon photovoltaic technologies and to develop fast, large-scale, cost-effective fabrication processes.' Rigid silicon-based solar panels are limited in their applications and there is reduced scope for improving efficiencies. Manufacturing silicon solar panels is costly and energy-intensive, requiring specialist equipment. Conversely, flexible inks or paints suitable for spreading onto any surface can be integrated into clothes, vehicles, buildings and any manmade object, and be fabricated using simple techniques.

The current two-year project is funded by the UK's Engineering and Physical Sciences Research Council. The current research is a continuation of previous research by Zoppi and Beattie, who are working with local SME Power Roll Ltd., specialists in thin film photovoltaics and photonic curing, plus Horiba Scientific from France, Hiden Analytical Ltd. and Liverpool University. Together, they: 'provide expertise in multiple spectroscopy measurements and analysis techniques,' Zoppi confirms.



Lightweight and flexible solar cell with increased power density

LAYERED FABRICATION

Zoppi explains: 'This project is based on creating photovoltaics from a multi-element compound containing copper, zinc, tin, sulphur and selenium, all of which are naturally abundant.' CZTSSe has an energy band gap ideal for absorbing most of the visible light spectrum, giving it great potential as a photovoltaic material. The best-performing photovoltaic films currently contain indium and gallium, both costly and rare elements. By using cheaper and more readily-available materials coupled with low cost and fast fabrication methods, CZTSSe-based 'solar paint' can be used on large areas such as buildings. The specific objectives of this project are to fine-tune the photovoltaic properties of the solar cells and to investigate fabrication techniques that do not involve the use of a furnace or vacuum equipment.

Most thin film photovoltaic compounds are created using vacuum techniques such as chemical vapour deposition or sputtering, which Zoppi says: 'are reliable and precise, but require costly capital equipment.' The process is also difficult to control for a compound comprising five elements. Instead, the group has developed a chemical fabrication method in which salts of copper, zinc and tin are dissolved in a flask from which air is excluded. Once degassed, a solution of sulphur is added at a temperature of around 220°C, resulting in a synthesised semiconductor fluid that is spin-coated or sprayed in layers onto a substrate such as molybdenum (Mo) foil.

The deposited inks are exposed to a selenium-rich atmosphere under inert atmosphere and high temperature to induce grain growth and allow selenium to diffuse into the ink. The solar cell is completed with layers of materials, including sulphide and oxide layers to provide the requisite properties and conduction matrix. Photovoltaic cells work by inducing an electrical current through a layered material by the action of photons. Two semiconductor materials with opposite polarities are sandwiched together, creating an electrical field at the interface. In semiconductors, negative and positive polarities are represented by materials that either contain spare electrons or electron 'holes', otherwise termed 'n' and 'p-type' conductors. When photons hit a layered solar cell, they cause spare electrons to move and thus, current to flow into the connecting conducting grid. In Northumbria University's nanoparticle solar inks, CZTSSe is the p-type absorber with a thin layer of cadmium sulphide being the n-type conductor.

OPTIMISING THE VARIABLES

The team has encountered many challenges. Zoppi mentioned that: 'In their as-grown form, the nanocrystals are not very efficient when completed into solar devices, despite being very good at absorbing photons.' The primary reason is the small size of the particles. This has been overcome through an annealing process in which the ink is heated to promote recrystallisation, resulting in the crystals growing to 100 times their former size. A further problem was the growth of a carbon-rich fine grain layer between the absorber and the substrate that, 'prevented the large columnar grains extending all the way to the metallic back contact and generated more losses of the photogenerated carriers,' according to Zoppi. This was found to be due to mixing the metal salts in a solution of oleylamine (OLA), which contains long carbon chains that diffuse to the back

> *Nanoparticle solar inks can significantly contribute to the world's energy needs and help address the problems of climate change*

of the CZTSSe layer during heat treatments rather than evaporate from the material. Other fluids were trialled and formamide (FA) removed the fine grain layer but resulted in a high-porosity film that was unsuitable for fabricating into a solar cell. Zoppi explains that, 'by layering films produced in OLA and FA, we were able to remove the fine grain layer and maintain the same device efficiency.'

Other challenges relate to the many variables that can be tweaked during the fabrication process. For instance, the ratio of the metals in the starting solution can be tuned, as can the temperature, reaction time and especially the cooling time, as each effects crystal size and texture of the nanoparticles. During selenisation of the CZTSSe ink, pressure, temperature and atmospheric conditions are all variables that affect final performance. The group has systematically investigated these variables and their effect on the final device performance and has found that the material is resilient to the presence of impurities, and in some cases, these can enhance performance. Zoppi says: 'One strand of research has examined selected impurities to understand how they affect the formation of the p-n junction in the solar cell device. We have investigated impurities from the starting chemicals used during the ink fabrication to those found in the substrate used (e.g. sodium (Na), chromium (Cr), iron (Fe) and many others).'

SIMPLIFIED MANUFACTURING PROCESSES

The final months of the project are aimed at undertaking the recrystallisation process without the need for a furnace and investigating fabrication methods that do not require vacuum technologies to lower costs, simplify and speed-up the manufacturing process. The transparent conductive oxide layer on the surface of the solar cells is deposited using expensive vacuum technology, and the team is now investigating a solution-based process, in conjunction with the North East Centre for Energy Materials.

Zoppi explains: 'One disadvantage of using a furnace for recrystallisation is that the whole structure, including the substrate, is heated to temperatures in excess of 500°C.' These temperatures are unsuitable for flexible substrates such as plastics and fabrics. The group is working with Power Roll Ltd. on the development of a photonic curing method using tuned broadband flash lamps to locally heat the CZTSSe layer in a fraction of second without affecting the substrate.

With solutions found to these final challenges, the project will have succeeded in pioneering flexible, cheap thin film photovoltaic technology that can be used on large areas and integrated into the design of cities. Currently, the highest efficiency achieved using the described fabrication process is around seven percent, however this is expected to improve with further fine-tuning. Even at this level, if the fabrication and materials costs are sufficiently low, Zoppi says: 'Nanoparticle solar inks can significantly contribute to the world's energy needs and help address the problems of climate change.' ●

Project Insights

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BIO

Dr Guillaume Zoppi is an associate professor in the Department of Mathematics, Physics and Electrical Engineering at Northumbria University, UK. After completing his PhD from Durham University on cadmium telluride photovoltaics, he joined Northumbria to focus on the exploration of novel semiconductors for electronic devices with emphasis on photovoltaics cells. His experimental research strengths combine fabrication, characterisation and assessment of thin film layers and devices.

Dr Neil S. Beattie completed a PhD in nano-physics at the University of Cambridge in 2005, sponsored by Toshiba Research Europe. Following his PhD, he worked as an innovation consultant for Innovia Technology on behalf of clients such as Shell, P&G, Boeing and Rolls-Royce. He joined Northumbria University in 2009 and is now an associate professor in the Department of Mathematics, Physics and Electrical Engineering. His research interests in semiconductor devices have led to development of quantum dot-based devices for ultra-high efficiency solar cells and the pursuit of Earth-abundant thin film photovoltaics materials.