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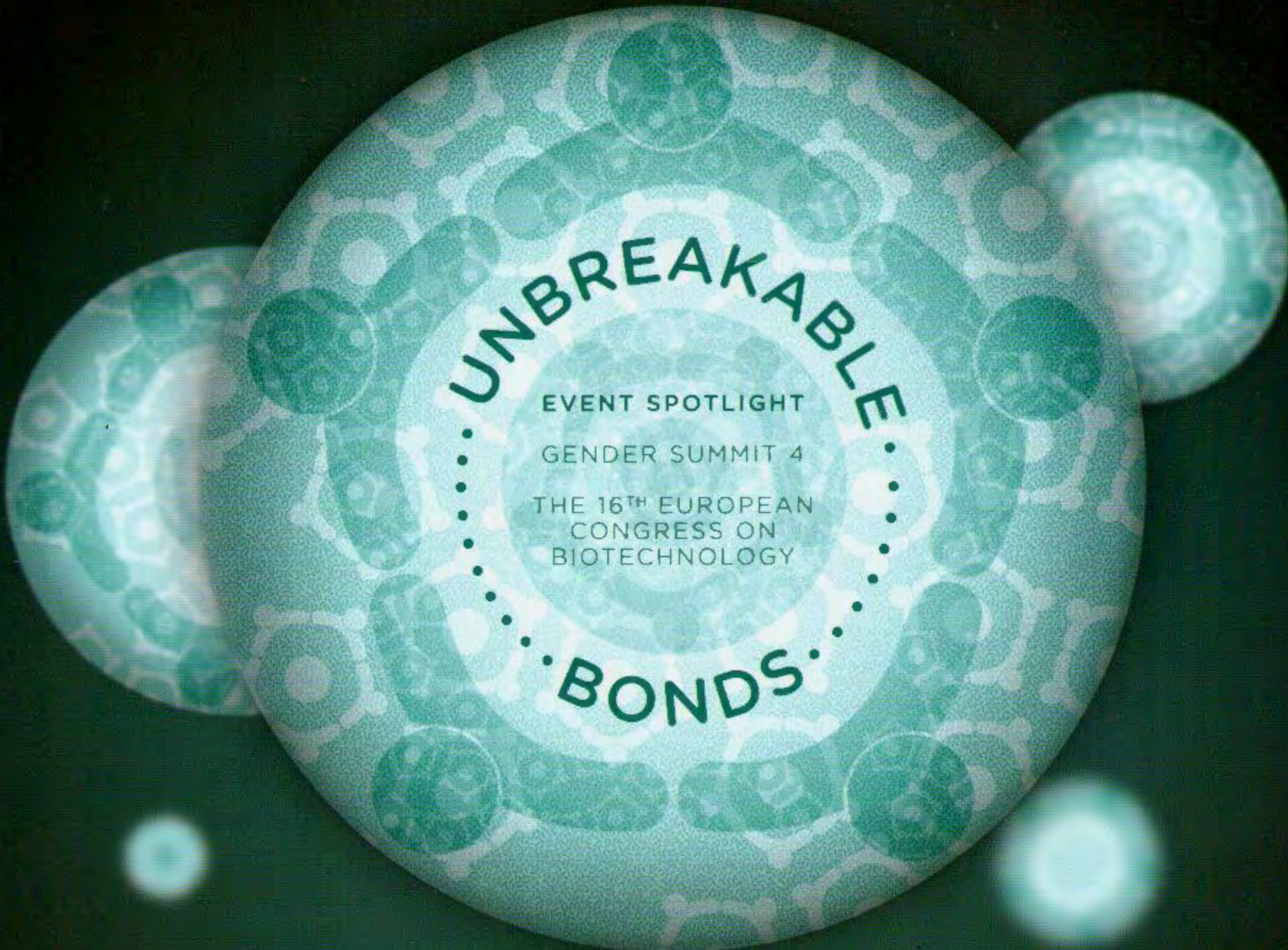

FOSTERING RESPONSIBLE SCIENCE WITH AND FOR SOCIETY

EXCLUSIVES

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Organisation for Economic Co-operation and Development

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Union for International Cancer Control

RESEARCH SPOTLIGHT

Nesta

Wellcome Trust

European Sociological Association

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International Planned Parenthood Federation

European Association for Chemical and Molecular Sciences

High potential

Dr Alexander Kuhn describes his group's ability to use bipolar electrochemistry to synthesise Janus particles on demand and on a large scale

Why is bipolar electrochemistry now a key concept within the field of nanoscience?

It wirelessly generates an asymmetric reactivity on the surface of conductive objects, allowing the highly controlled modification of objects with different materials in one step and on different parts of the object. This leads to multifunctional particles, like carbon nano tubes with metal at one end and a polymer at the other. The most appealing aspect is that modification can be achieved in the bulk phase, meaning that the concept can be scaled up for mass production.

What are the objectives of your research into asymmetric particles?

The primary objective is to demonstrate that bipolar electrochemistry is a fantastic tool to generate a huge variety of asymmetric objects and particles. We can produce almost any combination of materials, and we have spent the last few years demonstrating the versatility of this method. The only thing we can't do is modify insulating particles; however, as long as a particle is a conductor – or at least a semiconductor – we can deposit all kinds of materials, including metals, metal oxides, insulating polymers, conducting polymers, sol-gel and electrophoretic paints. We are now expanding to the modification of soft-matter, meaning that we will have explored nearly everything you can imagine in the field of materials science.

How do Janus particles differ from normal particles?

Janus particles are named after the two-faced Roman god, Janus. Each face has distinct physico-chemical properties, and this asymmetric surface composition allows two different types of processes to occur on the same particle. The simplest case is achieved by dividing the particle into two parts, each made of a different material or having different functional groups. This gives Janus particles unique properties that can be used for applications such as stabilising emulsions, medical imaging and bicoloured pigments in electrically switchable displays.

By what means will your work on Janus particles advance existing production processes?

If you look into the very abundant literature about Janus particles, you will see that in the majority of cases their synthesis involves the use of surfaces or interfaces to break the symmetry. This means that the production process occurs in a 2D reaction space, thus limiting the time-space yield.

Our process, based on bipolar electrochemistry, is one of the very few examples where Janus particles can be produced in the bulk phase of a reactor. Every single particle present in the volume of the solution will be modified in the same way very quickly. Typically, modification occurs in a couple of seconds. We believe that bipolar electrochemistry is a serious alternative for mass production of Janus particles and will ultimately stimulate their use for applications that have not been thought of yet.

Can you describe the reactor you use?

The design of our reactor has evolved greatly over the last few years. In the beginning, we were using reactors with very small volumes in the millilitre range for proof-of-principle studies. With the financial support of Aquitaine Science Transfer (SATT) and the French National Research Agency (ANR), we developed a bigger reactor based on our patented concept (100 ml). To further increase production rates, we then went from a batch reactor to a semi-continuous flow-through reactor. This allows us to produce gram quantities of Janus particles. Depending on the requirements of an industrial partner, we first produce particles at this scale for testing their properties. If they satisfy the client's criteria, we can then develop a bigger reactor and create large quantities of the particles in collaboration with the company.

Could you shed some light on your technology transfer service, BrivaTech?

It was founded in January 2014 and employs two chemical engineers. It is devoted to promoting 'the know-how' of our group and establishing partnerships with companies to transfer our technology from the academic world to industrial reality. BrivaTech can synthesise generic particles and co-develop custom-made particles, which can then be produced either by BrivaTech, or by the customer under a licence agreement.

Has collaboration played a role in your activities?

Our group has a large international collaboration network. Collaboration was crucial for the development of the bipolar electrosynthesis of Janus objects. As our technology has now reached a satisfying state of maturation, we are opening up our collaboration scheme to interested industrial partners.

True bulk synthesis of Janus particles

The Analytical Nanosystems group at the **Institute of Molecular Sciences** of the **University of Bordeaux** has used the capabilities of bipolar electrochemistry to manufacture versatile micro- and nanoparticles that have different properties on their opposing sides, thus allowing the rational design of complex micro- and nanoscale objects

SYMMETRY IS PRESENT everywhere in the natural world; for example, in the radial symmetry of snowflakes, the fractal symmetry of Romanescu broccoli and the mirror symmetry of the Milky Way. However, often it can be quite beneficial for a certain number of applications to break or lower the symmetry of systems and items. In this context there is a particular class of objects called Janus particles that scientists have designed to be asymmetric through the use of bipolar electrochemistry.

The concept of bipolar electrochemistry has existed for years, and in the past, scientists have applied it to tasks such as water splitting and increasing fuel cell performance. Recently, however, it is receiving attention for its utility in the field of micro- and nanomaterials. The technique induces bipolar redox reactions on a substrate under the influence of an external electrical field; if the triggered polarisation effect is sufficiently strong, the redox reactions at opposite ends of the substrate can then cause the deposition of a selected material on one end, either leaving the other end structurally unchanged, or depositing a second material on the opposite side. For this reason, Janus particles have huge potential for multifunctional material applications in many contexts.

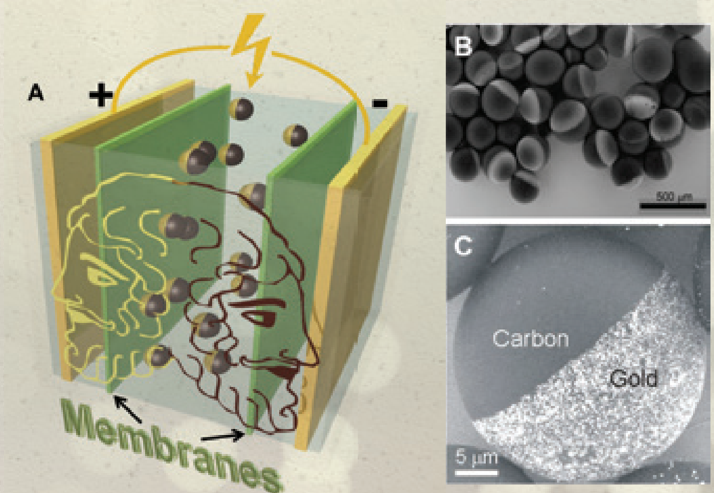
THE BEAUTY OF BIPOLAR ELECTROCHEMISTRY

Since the first report of the synthesis of Janus particles, scientists have developed many processes for their production. However, the majority of these processes rely on the use of interfaces or surfaces to break the symmetry of the object; since they are based on 2D reaction spaces, they are merely capable of producing monolayer quantities of particles. Having conducted a comprehensive analysis of these techniques in 2012, the Analytical Nanosystems group of the Institute for Molecular Sciences at the University of Bordeaux, France, concluded that most of them were not robust, practical or cost-effective enough for industrial scale production. Moreover, the techniques were not sufficiently versatile or adaptable for breaking the symmetry of different types of particles. In a search for ways to achieve the inherently difficult task of breaking the natural symmetry of particles, the group adapted the concept of bipolar electrochemistry.

For Dr Alexander Kuhn – the coordinator of the Janus particle project in the group – the beauty of bipolar electrochemistry is that it enables the simultaneous transformation of thousands or millions of tiny micro- and nanoscale objects into dissymmetric or asymmetric forms. "Objects can be precisely engineered to have identical, very attractive new properties," he enthuses. Another major benefit of the approach is that it is possible to control the modification of a substrate without physically connecting it to an electrode or employing any intermediate surface or interfacing agent. The substrate can simply be suspended in a solution of metal salts or monomers during the reaction.

THE JOURNEY TO LARGE SCALE

In 2008, Kuhn engineered the controlled deposit of gold on one of the two ends of a carbon nanotube. The application of a strong electric field to the solution around the nanotube caused its polarisation, so one end was excessively negatively charged and the other excessively positively charged. This induced an electrochemical potential difference between the two ends that resulted in the reduction of



A. Schematic illustration of the bipolar electrochemical reactor

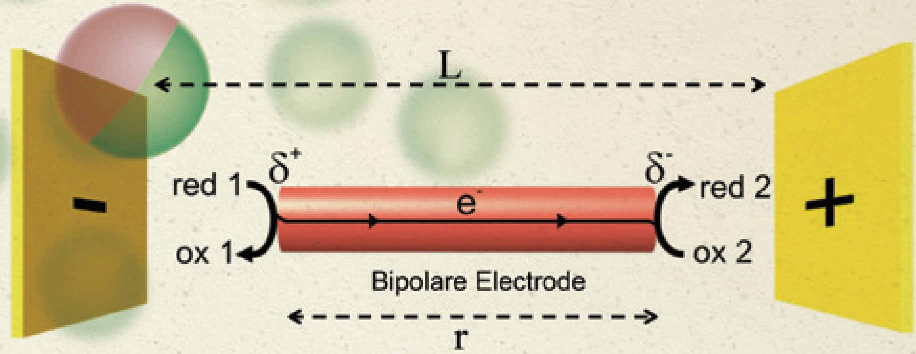
B. Batch of synthesised Janus particles

C. Magnified Janus particle consisting of carbon modified with a half-sphere of gold.

APPLICATIONS OF ASYMMETRY

Using bipolar electrochemistry to break symmetry in physical, chemical and biological systems has applications in many fields. For example, it can be utilised in:

- Electronic paper display
- Nanoelectronics
- Chemical catalysis
- Medicine
- Stabilisation of emulsions
- Photovoltaics
- Photosplitting of water



Schematic illustration of the concept of bipolar electrochemistry. A conducting object is placed in a solution between two feeder electrodes and the application of a voltage between these electrodes leads to a polarisation of the object, allowing it to carry out two different chemical reactions on its opposite sides.

the metal salt on one side of the nanotube, and caused the oxidation of water on the other. The result was a gold-tipped 'nanomatch'. From this, Kuhn varied the time that the nanotubes were exposed to the electric field to obtain nanomatches with different size heads.

Kuhn and his team then experimented with breaking the symmetry of objects of different compositions, sizes and shapes. They found that their method supported the combination of a large variety of materials irrespective of dimensions or geometry, as long as the materials were capable of polarisation. They named the 3D technique Capillary Assisted Bipolar ElectroDeposition (CABED) and have convincingly proved that it allows selective modification of surfaces and localised modification of objects. CABED is a single-step technique capable of modifying isotropic or anisotropic particles with deposits, including insulating or conducting polymers and semiconducting metal oxides. The process takes seconds, is highly controllable and also relatively inexpensive.

CABED can also break the symmetry of many particles simultaneously, so it can be scaled to industrial production of identical Janus particles. This ability has led to the next phase of Kuhn's work. In a project funded by the French National Research Agency (ANR) called PROJANUS, Kuhn and the group are now developing a reactor for synthesising larger quantities of Janus particles. Through the project, the Analytical Nanosystems group has also established a technology transfer service for interested industrial companies: "We will be able to offer asymmetric particles to industrial partners that are specifically tailored to their needs," Kuhn explains.

The objectives of the PROJANUS project are:

- To develop and test an industrial reactor that can synthesise several kilograms of Janus particles at the same time
- To form collaborations with interested industrial through the creation of a start-up

PROGRAMMED PROPULSION OF NANO-OBJECTS

The use of high voltages in bipolar electrochemistry has led the researchers to some interesting discoveries in terms of Janus particles and propulsion. When a strong electric field is applied to metallic micro-objects in suspension, it can push them towards the anode end, because as one end dissolves the other increases in length. Thus, the objects' decomposition acts as a 'fuel', propelling them in a specific direction at a speed up to 100 $\mu m s^{-1}$. This is an important discovery as this self-perpetuating propulsion removes the need for any form of classical combustion material. Kuhn sees possibilities for this phenomenon in nanomedicine and nanomechanics; for example, it could replicate natural systems, such as the movements of bacteria, or act as micromotors. "This aspect of bipolar electrochemistry is more for fun – we play with new concepts to develop these 'swimming' objects," Kuhn enthuses. "Very recently, we've been able to integrate electronic devices into the swimmers that are also fuelled by bipolar electrochemistry, so we have started to think about swimmers with real functionality." In fact, Kuhn and his group have integrated several items – including light-emitting diodes and temperature sensors – into the swimmers. "The integration of any miniaturised device, such as a pH sensor or a microphone, would be just as easy. We think that there is a promising future for this technology."

INTELLIGENCE

PROJANUS

PRODUCTION PROCESS OF ASYMMETRIC PARTICLES USING BIPOLAR ELECTROCHEMISTRY

OBJECTIVE

To establish bipolar electrochemistry as a competitive alternative to synthesise asymmetric micro- and nano-objects – called Janus particles – for a large variety of materials combinations in the bulk phase of a solution.

KEY COLLABORATORS

Professor Jumras Limtrakul; **Dr Chompunuch Warakulwit**, Kasetsart University, Thailand

Professor Paolo Ugo, University of Venice, Italy

Professor Darren Bradshaw, University of Southampton, UK

Professor Neso Sojic; **Dr Laurent Bouffier**; **Dr Dodzi Zigah**; **Dr Valerie Ravaine**, University of Bordeaux, France

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ALEXANDER KUHN is a professor in the Institute of Molecular Science at the University of Bordeaux, France, specialising in electrochemistry, surface modification and nanoscience. In recent years, he has worked with bioelectrochemistry, electroanalysis, the rational design of electrode surfaces and the synthesis of micro- and nano-objects that can be used for applications ranging from catalysis to autonomous swimmers.