Sparks fly in nanoscale engineering

Dr Carole Rossi and her collaborators at the Laboratory for Analysis and Architecture of Systems in Toulouse, France, as well as contributors from around the globe, are engineering nanoscale reactive materials. Coupling techniques used in the manufacture of microchips to the reactive chemical properties of metal oxides, the team are able to create atomic layers of reactants which have the potential to revolutionise our understanding of energetic materials.

Since studying for her PhD, Dr Rossi has been interested in the 'sleeping' power of chemical energy and its potential for fast delivery of energy. Since the invention of gunpowder, scientists have understood the power of mixing potent reactants in close proximity ready for ignition and this arguably entered the nanoscale when chemists began synthesising molecular explosives such as nitroglycerine and trinitrotoluene (TNT). Bringing the required atoms into close molecular contact allowed for a massive increase in reaction speed and subsequent energy release. Dr Rossi recognised that, with modern manufacturing techniques, turning this devastating energy to small-scale practical purposes was a realistic possibility.

Despite significant advances in the field of energetic materials (EM) manufacture, traditional EMs struggle to fulfil their potential at the micro scale. Due to intrinsic energy losses and the relatively slow reaction rate, they experience quench (the process stalls for lack of sufficient energy transfer) in even relatively large volumes such as steel and glass tubes of millimetre-scale diameters. For these applications, more energetic materials are required which can overcome the high energy demand of micro- and nanoscale systems. Dr Rossi noted that some successes have been recorded by integrating metal particles, particularly aluminium (Al), to the propellant mixtures to increase the reaction rate.

THE CHALLENGES OF SCALE

Aluminium is particularly suitable for this role due to its rapid oxidation. Small particles, commercially available at low cost, are intrinsically stable due to their oxide coating. They increase the reaction rate through thermal transfer, a function of their high thermal conductivity. Dr Rossi evaluated that peak efficiency is reached when Al makes up 20% of the total propellant. This 'doping' of propellants improves conditions at the mesoscale (mm–cm), but is not sufficient to overcome thermal losses at the microscale.

Despite several approaches investigating the use of alternative doping agents such as carbon nanotubes, or synthesis of nano-propellants, or a combination of the two where the propellant is encapsulated within carbon nanotubes, Dr Rossi and others believe that an alternative solution exists.

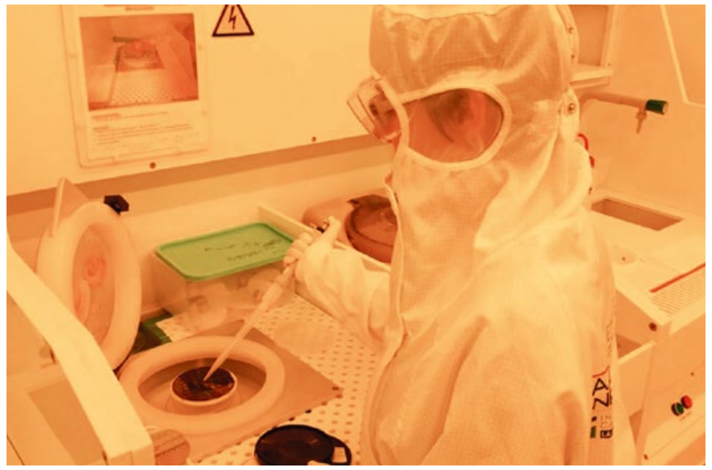
AN OLD TECHNOLOGY REPURPOSED

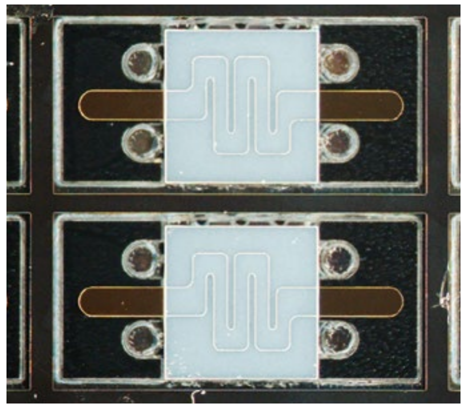
Thermite reactions have long been known for their powerful thermal properties, being put to such heavy-duty uses as welding railway tracks together. In these reduction-oxidation reactions a metal fuel, usually Al, is mixed with a metal oxide and brought to reaction temperature. The Al, which makes stronger and more stable oxygen bonds than its companion metal oxide, essentially steals this oxygen to do so, releasing a large amount of heat in the process. Dr Rossi and others have noted that this reaction, in contrast to those of traditional propellants and explosives, increases in speed and energy density as the materials are scaled down towards the nanoscale. Speed in particular can increase by a factor of ten when particle size is reduced from 20,000nm to 50nm, with ignition time decreasing by more than two orders of magnitude (from seconds to tens of milliseconds).

LAYERING THE FOUNDATIONS

Manufacture of suitable mixtures of these materials has proved complex, however. Sonic mixing of nano-powders in solution and the creation of gels by a similar method ▶

> **Thermite reactions, in contrast to those of traditional propellants and explosives, increase in speed and energy density as the materials are scaled down towards the nanoscale ”**





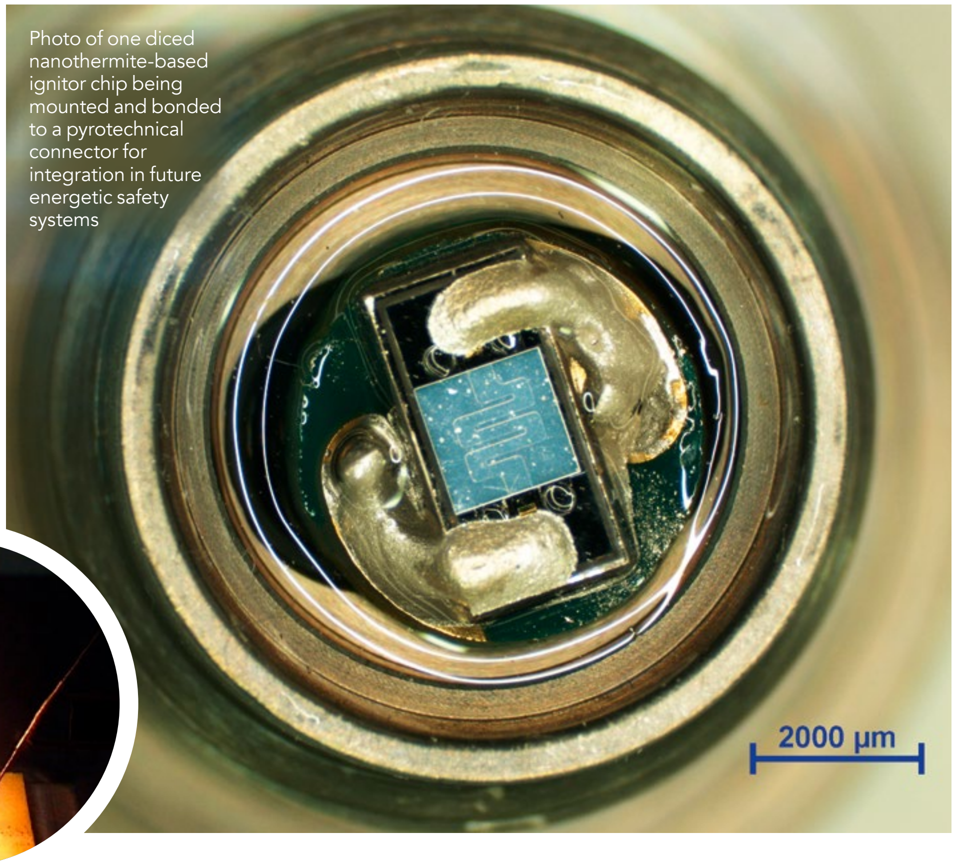
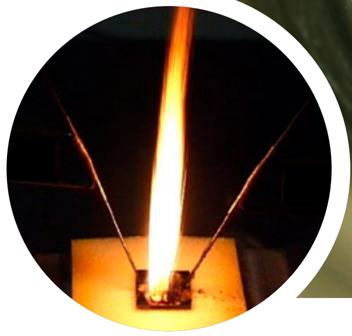


Photo of one diced nanothermite-based ignitor chip being mounted and bonded to a pyrotechnical connector for integration in future energetic safety systems

Above: Photograph of two nanothermite-based ignitor chips: white squares are Al/CuO nanoscale reactive film made of hundreds of alternating Al and CuO nanolayers; yellow rectangles are the gold electrical pads used to supply the electrical energy for the nanothermite ignition. Total dimensions: 3.8 ×1.8 mm²



Right: Photo of a flame generated by the reaction of Al/CuO nanoparticles mixed with PTFE nanoflakes

are limited by their ability to provide a sufficiently uniform mixture without impurities. More promising techniques have focussed on the deposition of alternate layers of the constituent elements, utilising methods common in the manufacture of electronic components. These overcome the limitations of mixing by exploiting precise control of the layer thickness (concomitant with particle size) and the elimination of impurities (often being performed under vacuum or in inert gas atmospheres). Nano-structuring of silicon, production capacity for which already exists in the semi-conductor market, has also proved effective in bringing oxides into close contact with potential fuel metal.

PROBING DEEPER

Although the functional properties of these new EMs has been well investigated, the detailed understanding of their underlying principles, and therefore the ability to generate theoretical models of novel materials, has not. Dr Rossi and her collaborators are focusing on probing the interfacial layers, the region where reactive layered nanostructures meet, and the core of their function.

Using model surfaces created by atomically precise deposition methods, the team are able to derive detailed information through advanced imaging of the atomic structure. This approach allows them to assess the contribution of the interface layer between Al and the metal oxide to the reaction kinetics, as well as to the intrinsic stability of the material.

OUT IN THE REAL WORLD

With the goal of developing an atomic level understanding of the interface formation process, they are utilising cutting edge technologies for the modelling, creation and investigation of this layering approach to EM manufacture. The team will thus be able to transform the optimisation of this process, further refining a field which has seen rapid progress in recent years as the scale of operation has shrunk down from the meso- to truly nanoscale manufacture of EMs.

This work is vital to support the expanding field of microelectromechanical systems, where actuators and precisely localised thermal power generation are incorporated into a range of modern micro-electronic devices. From the microinjection of pharmaceuticals, to weight-critical propulsion systems in the space industry, the requirement for digitally controlled and precisely engineered EMs is growing. This is not to mention the challenges of manufacture of increasingly small-scale devices, where precise soldering and welding of components is vital to their operation. It is clear the work that Dr Rossi and her colleagues are doing, to uncover the atomic principles underlying these advances, is laying the foundation for fundamental changes in our understanding of highly energetic materials.

> **The team are utilising cutting edge technologies for the modelling, creation and investigation of this layering approach to energetic materials manufacture**

Q&A

What is it about atomic scale engineering that fascinates you?

I've always had a strong interest in the nanoscale world. As a student, I was fascinated by both the difficulty of appreciating the smallness of nanoscale and the fact that this scale defies the common sense of understanding. Atomic scale engineering not only gives new ways to see the matter, but it explores a wide range of methods to interact with atoms or molecules, to provoke their self-assembly on atomically well-defined surfaces and structures. Once the mechanisms controlling the self-ordering phenomena are fully understood, the self-assembly and growth processes can be steered to create a wide range of surface nanostructures from metallic, semiconducting and molecular materials. This offers something magical: we can redefine a new world just by organising atoms differently.

Why did you focus on micropyrotechnics?

During my PhD, I developed a keen interest in micropyrotechnics – they seemed a huge and powerful source of chemical energy that can be delivered very quickly. I imagined many devices that could provide high energy actuation within a very tiny volume.

What are the principal real-world applications for EMs?

Pyrotechnics are single-use devices containing energetic materials with a wide range of applications – the most famous example is air bag inflators. For three decades, many pyrotechnic applications have appeared with the apparition of new energetic compounds: biological neutralisation, brazing of materials and pressure-mediated molecular delivery. Safety devices, such as tiny pyrotechnics actuators, can now close a door in case of fire, while wireless pyrotechnic devices can even protect against avalanches.

With the growth of energetic materials in society, new challenges accompany the development of new energetic materials and pyrotechnical systems. Among them is the necessity to engineer a class of safe and green energetic materials that can be programmed for designed missions.

How do you see the EM field developing?

Until recently, most energetic nanomaterials research has focused on enhancing the surface area, maximising the intimacy between reactive components, increasing the reaction rate and decreasing the ignition delay, while at the same time improving safety. For a decade, new insights into the atomic scale description of interfacial regions and new capabilities in surface functionalisation have provided alternative ways to control the nanomaterial thermal decomposition and sensitivity.

By manipulating the reactive matter and its interfaces at the nanoscale, we can now easily produce targeted effects that cannot be achieved dealing with bulk materials only. These new categories of multi-functional energetic mixtures are expected to lead to major breakthroughs in propellants, explosives, pyrotechnical devices and weapons and will also constitute a breakthrough technology for national security by proposing fully integrated smart passive devices that can remain in sleep-mode for tens of years & wake up within nanoseconds.

The potential impact of future advanced energetic materials and pyrotechnical systems are eagerly anticipated. However, we are still struggling to translate the fundamental advances reported in scientific literature into tangible applications.

What are the benefits and challenges of international collaborations?

Since I began my career, I have benefitted greatly from interdisciplinary collaborations. Innovation at the nanoscale requires an integrated and synergistic approach based on theory, experiment and technological developments. To this end, I want to stress the effort I have put into integrating critical collaborations with theorists in my lab (A Estève) and with experts in the characterisation of nanoscale mechanisms (Y Chabal, UT Dallas). The collaboration with chemists is also crucial as many of our engineering processes use wet-chemical processes. Close collaboration is required to bring together the host of characterisation techniques, theoretical modelling and the deep chemical insight developed by colleagues over the past two decades.

Detail

RESEARCH OBJECTIVES

Dr Rossi's research focuses on designing nanoscale reactive components (vapour deposited nanolayer and oxide or metallic quantum dots), assembling them into scalable 3D structures and finding the best nanotexture and nanomorphologies for achieving high energetic and rapid reactions.

FUNDING

- ANR
- CNRS-INSIS
- University of Toulouse/IDEX

COLLABORATORS

- A Estève (LAAS)
- Y Chabal (UTD, USA)
- C Tenailleau, P Alphonse (CIRIMAT)
- B Warot Fonrose (CEMES)

BIO

Dr Rossi completed her PhD at the University of Toulouse under the guidance of Dr Esteve and undertook her post-doc at the University of Berkeley. She has been a research scientist for CNRS since 1998 and is now Director of IMPYACT joint laboratory between LACROIX and LAAS and Co-Director of Joint international lab, ATLAB.

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