Renewing and upscaling SA's nanomaterials initiatives

Research into nanomaterials in South Africa was formalised in 2005 with the publication of the National Nanotechnology Strategy and its 10-year plan, but there remains a need for technologies to be developed and employed for large scale local manufacture of these materials. SAIChE IChemE President, David Lokhat compiles a technology overview.

ack in 2005, South Africa was one of the few developing economies in the world to realise the potential of nanomaterials when the South African Nanotechnology Strategy and its associated 10 year plan were put into effect.

Water, energy, health care, chemical- and bio-processing, mining and minerals, along with advanced materials and manufacturing were explicitly identified as application specific areas to benefit from the programme and, while the technology's contribution to the development of the country has been questioned, there is no doubt that valuable research has since been done.

Technical projects brought to completion or in progress include: synthesis of nanoparticles; development of better and cheaper solar cells; nanophase and electro-catalysts; fuel cell development; synthesis of quantum dots; composites' development; and atomic modelling, to mention but few.

Projects are being carried out at eleven universities; four research organisations and several private sector companies in fields from mining and surface coatings to paper manufacturing. Moreover, almost every major university in the country has a dedicated nanotechnology or nanomaterials platform, which connects researchers and academics with funding agencies, industrial partners and other stakeholders, in order to carry out fundamental and applied research.

South Africa has innovation centres at the CSIR and MINTEK, which have each developed collaborative research programmes with other national institutions: in the design and modelling of novel nano-structured materials (at the CSIR); as well as the application of nanotechnologies in all targeted fields of the nanomaterials strategy.

AuTEK Biomed, a collaborative project between the gold mining industry and MINTEK is creating gold-based chemo-therapeutics for treating diseases such as cancer, malaria and HIV & AIDS. The Rand Refinery hopes to build a nanotechnology plant if ongoing experiments prove gold nanoparticles can be used as catalysts for detoxifying air in our mines; while paper manufacturer, Sappi, is currently investigating the possibility of using nanotechnology to monitor temperature, termites and fungus in its tree plantations.

Global applications

Back in 2010, 1 317 consumer goods taking advantage of the unique properties of nanomaterials were already estimated to be in the global market. This number has steadily risen every year. Many of these early products used silver nanoparticles for antibacterial purposes. Carbon in the form of carbon nanotubes and titanium oxide were the second and third most adopted nanoparticles, while the remaining products contained either non-



The chemical vapour deposition (CVD) process involves precursor gases being delivered into the reaction chamber at approximately ambient temperatures. As they pass over or come into contact with a heated substrate, they react or decompose forming solid nanoparticles that and are deposited onto the substrate (boat)

specific chemicals, nanofilms or nanoscale wax particles. Approximately 450 of the 1317 products available in 2010 were personal care products: cosmetics, sunscreens or textilerelated materials.

Some of today's common uses for nanomaterials include:

- Non-scratch glasses that use ultra-fine polymer films with protective and antiglare properties.
- Building materials such as cement, tiles, grouts, sealants and windscreen glass that are coated with nanoparticles of titanium oxide to give advanced performance such as self-cleaning and anti-bacterial properties.
- Clothes with advanced properties such as UV blocking, infrared reflecting, antibacterial, crease-proof, stain-resistance, water-repellence, moisture-control, flame-retardant, odour removing, antistatic, electric conductivity, heat retaining, temperature regulating, wrinkle resistance and high mechanical strength. Examples include ties that repel dirt, shirts that do not need ironing, or skiing anoraks that use nanofibres to resist water and wind.
- Automotive and aerospace technologies where nanoparticle additives in engineconstruction materials are used for lighter weight, higher strength, improved temperature/corrosion resistance and superior wear resistance. Metal oxide nanoparticles and carbon nanotubes and fibres (CNTs and CNFs) are used as additives in polymer nanocomposites for densification, improved mechanical strength and to improve the wear resistance of structural materials and tyres.
- In sports equipment such as tennis rackets, CNTs are used to make them lighter, more flexible and more resistant.
- More effective and protective cosmetics: lotions granulated to below 50 nm that let light through, giving a purer, cleaner feel; anti-wrinkle creams that use polymer nanocapsules to distribute active agents such as vitamins more efficiently; sun creams that use nanoparticles of titanium dioxide and zinc oxide, so they do not turn white when spread on the skin, while still offering the same degree of protection against UV light as traditional creams.
- Silver nanoparticles used as an antibacterial agents in many consumables, ranging from surgical instruments and household appliances to pet food bowls.

Some applications of nanomaterials that are close to industrialisation level include:

- Hydrogen storage using metal or ceramic nanostructured materials.
- The delivery of pharmaceuticals in nanocapsules via hollow nanoparticles such as fullerenes.

- Catalysts, adsorbents and absorbents as nanoporous materials: in vehicle filters for reducing environmental pollution and fuel consumption, for example.
- · Nanoscale electronic and optical instruments (nanocables).
- Environmental protection: dendrimers exhibiting a high degree of surface functionality and versatility can act as 'attractors' of metal ions.

There are, of course, many other applications of specific nanomaterials under investigation.

Production methods for nanomaterials

Bottom-up approaches for the production of nanoparticles include vapour phase techniques such as aerosol spraying onto heated surfaces to trigger a pyrolysis reaction for the creation of nanoparticles such as carbon black pigment particles and titania. These have uses as reinforcement in car tyres and for the production of paints and plastics. An electrospraying process at room temperature has also been developed at Oxford University for the production of semiconductors and metal nanoparticles.

Atomic or molecular (gas) condensation in a vacuum chamber is the oldest production method. Used mostly for metals, the material is heated to below its boiling point in a vacuum so that atomised/vapour particles are produced. These are then carried into an inert gas atmosphere where they condense, forming spheroidal solid nanoparticles.

Electrical techniques such as arc discharge; laser ablation; and plasma processes are also being developed, but the most promising vapour phase technique for large scale production is probably chemical vapour deposition (CVD), which is widely used for the production of CNTs.

CVD offers many advantages: uniform thickness of coatings; flexibility of chemical precursors -70% of elements in the periodic table have been deposited - and an ultra-high vacuum is not required for nanoparticle production. CVD processes involve safety issues and health hazards, however. Also, despite being a flexible method, CVD requires numerous experiments to establish growth parameters. Liquid phase production techniques

include:

- The Sol-gel method, a long established industrial process for generating colloidal nanoparticles from the liquid phase. The process is based on hydrolysis or condensation reactions. With the correct amount of reactants, nanosized particles precipitate.
- The Solvothermal method is used for crystalline solids. Solvents well above their boiling point are used in enclosed vessels. High autogenous pressures are supported



and the organic solvents are used to disperse non-oxide nanocrystallites and to stabilise metastable phases.

- Hydrothermal synthesis: a subset of the Solvothermal method, this is an enabling and underpinning technology that is ready to prove itself at industrial scale as a result of recent breakthroughs in reactor design. The process involves mixing superheated/ supercritical water with a solution of a metal salt.
- Sonochemistry: a research area in which molecules undergo chemical reaction due to the application of powerful exposure to ultrasound.

There are also a number of top down approaches to nanomaterial production, including: mechanical attrition such as milling and mechanochemical processing; hybrid approaches such as nanolithography using electron-beam, focused ion-beam writing, proximal probe patterning, X-ray lithography, scanning probe microscopy (SPM) and others. Template fabrication is one of the most popular and maybe cheapest methods of nanolithography and used for the growth of nanowires by electrodeposition, for example. Templates of ordered nanopores have to be made before the pores are filled using one of the bottom up process options - electrodeposition; the sol-gel method or chemical or physical vapour deposition.

These and many other potential processes offer enormous opportunities for South African researchers to develop industrial scale processing plants as part of the initiative to grow a modern locally based nanomanufacturing industry.

Challenges and future outlook

As with any new technology, there have been concerns that the very properties of nanoparticles that render them so useful may also cause undesirable health effects. The assessment of potential risks of nanotechnology is at an early phase of development. Technologies and practices that eliminate or prevents potential unintended effects to



High definition transmission electron micrographs of copper and iron oxide nanoparticles synthesised in the chemical engineering laboratory of UKZN using a simple precipitation method.



Vapour and liquid phase techniques are the leaders for large scale production of inorganic nanoparticles (ref: http://nanoparticles.org/ standards/).

workers, consumers and the environment will be of critical importance going forward.

Research in this field needs multi- and intra-disciplinary specialists: toxicologists, environmental scientists, nanotechnologists, risk assessors, epidemiologists and others. The results of such studies will be vital if we are to support and enable industry-scale manufacturing of nanotechnology-based products in South Africa.

While National Nanotechnology Strategy projects were expected to reach maturity within 10 years and result in viable commercial products, it was soon realised that although the base level technologies and prototypes were successful, true commercialisation would require further development of the manufacturing methods. This is now a key focus area and that which requires continued public and private sector support.

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