Nanocoated particles make material advances

Wendy Laursen looks at the benefits of a new coating process

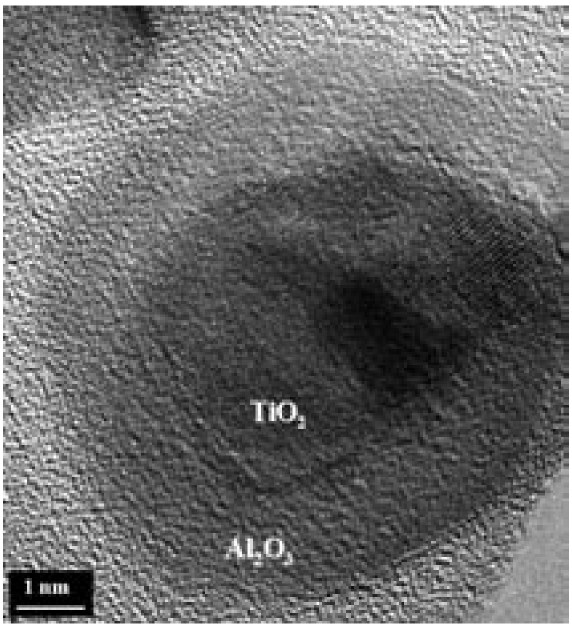
Coated nanoparticles can retain their bulk properties even though their surface characteristics are modified. They are increasingly being used to solve problems of chemistry mismatch, thermal management, and structural integrity.

Professor Alan Weimer from the University of Colorado, Boulder, USA, leads a team of researchers that has developed a technique that solves the problems and limitations associated with the commonly-used chemical vapour deposition (CVD) method of coating particles. The platform technology he has developed is opening up possibilities for new materials across manufacturing, electronics, and military markets.

CVD is a coating process in which gaseous reagents are used to create a film on materials. It has been used to great effect particularly in the manufacturing of semiconductors, but has limitations. For example, there is no inherent control of the film thickness as its growth is dependent on reaction time, flux of reactants, and reaction temperature. In addition, competing gas phase reactions can produce nanoparticles that are scavenged, resulting in granular films, while precursor feed rates are limited by particle mixing times.

Using a fluidising bed reactor, Weimer and his team have successfully coated a variety of nanoparticles using atomic layer deposition (Particle ALD). He says that Particle ALD has significant cost/performance benefits over CVD as it can be operated with virtually no waste of precursors and can place perfect nano-thick films on high surface area particulate substrates.

Cross-section HRTEM Image of an Al_2O_3 (15 Å) ALD-coated 7 nm TiO_2 nanoparticle processed in a fluidised bed reactor (source LF Hakim et al, J Amer ceram soc, 89, 3070 (2006)



Particle ALD allows finer particles to be coated than does CVD, which is typically limited to particles larger than about 10 µm. This is because van der Waals forces cause smaller particles to fluidise as aggregates which are "glued" together by the CVD processing.

The ALD technique uses self-limiting surface chemistry to control film thickness and produces conformal, non-granular, pinhole-free films on primary particle surfaces. Films can be as thin as 1 Å thick. Deposition is independent of line-of-sight, no competing gas phase reaction occurs, and nearly 100% of the precursor is used, greatly reducing waste.

ALD differs from CVD because the ALD reaction is split into two surface half reactions. Having two sequential steps means the surface will react with each reagent only until it is completely coated with a new atomic layer. Once this occurs, no more reactions will take place, making it self limiting. New functional groups are then in place for reacting with the second reagent. The steps can be repeated until the desired film thickness is achieved.

Deposition of alumina films has been demonstrated for alternate binary reactions involving trimethylaluminum ($Al(Ch_3)_3$) and water vapour. The reaction in equation 1 is split into two parts as shown in equations 2 and 3.

$$2Al(CH_3)_3 + 3H_2O \rightarrow Al_2O_3 + 6CH_4 \quad (1)$$

$$2AlOH^* + 2Al(CH_3)_3 \rightarrow 2[AlOAl(CH_3)_2]^* + 2CH_4 \quad (2)$$

$$2[AlOAl(CH_3)_2]^* + 3H_2O \rightarrow Al_2O_3 + 2AlOH^* + 4CH_4 \quad (3)$$

Note: The asterisks designate the surface species.

Bulk processing occurs in a fluidised bed reactor as it provides good control of the contact between particles and reactant gases as well as control of temperature, pressure, and flow conditions. The system can be kept at low pressure by using mechanical vibration to improve the fluidisation. The technology is automated and has batch processing functionality that has already been widely used in the food, pharmaceutical, and energy industries.

Weimer's research team has verified the technique's ability to coat particles completely and uniformly. The scientists have coated a number of different particle sizes and types including silica, zirconia, titania, high density polyethylene (HDPE), and iron oxide particles, under a range of pressure conditions.

Particle image analysis was used to study the aggregation properties of the nanoparticles as they fluidised. A laser was coupled with a monochrome digital camera using a standard charge-coupled device to obtain images from the splash zone of the fluidised bed. This enabled real-time analysis of individual aggregates while ensuring that the particles examined were characteristic of those in the bed.

The fluidised aggregates displayed a dynamic behaviour that contrasted with static agglomeration caused by settling. The outer edges were shed and then picked up by other aggregates and this continual break-up and reforming enabled bulk ALD processing to completely coat the individual particles.

No sintering between particles was observed as the aggregation was physical in nature and not caused by the coating process.

The completeness of the coating process was confirmed using Fourier-transform infrared spectroscopy. The frequency of the vibrational modes for the coated particles matched that of alumina powder and no spectra for the substrate particle appeared.

Weimer and his team were the first in the world to use ALD particle processing, and the University of Colorado holds key patents for the technology. ALD NanoSolutions was founded by Weimer, Karen Buechler, Steven George, and Michael Masterson and has exclusive rights to practise and to sublicense Particle ALD worldwide. The company is commercialising the technology across a variety of applications.

A number of innovations in electronics promise strong marketing opportunities for the company. Electronic components are protected from damage by glob-top packaging typically made from boron nitride or aluminium nitride. These materials are electrically insulating and have high thermal conductivity making them good as fillers to improve heat transfer in microelectronic packages. They have some limitations, however. Aluminium nitride reacts with water and boron nitride is so inert that it does not easily disperse in the epoxy matrices it is used with, reducing thermal conductivity in the end product. Coating the boron nitride with an alumina film (Al_2O_3) using ALD improves the rheological properties of the epoxy without significantly reducing its thermal conductivity.

The failure of electronic devices caused by lightning strikes, electromagnetic pulses, and other transient events causes billions of dollars of damage annually and the miniaturisation of electrical components only tends to increase the risk. Weimer believes the ability to change the surface properties of metal substrates without compromising their bulk properties will help solve this problem. Nanocoating the particles with insulating materials such as alumina or silica produces a composite that could be embedded in a moldable polymeric binder to produce a new class of metal insular varistors. These varistors should have sub-nanosecond response times and a highly nonlinear dependence (quantum tunnelling) with respect to applied voltage, thus providing high voltage surge protection.

The increasing miniaturisation of multilayer ceramic chip capacitors for electronic devices is leading to increasing difficulty in producing the dielectric layer. $BaTiO_3$ particles are mixed with other particles, and at very small thicknesses the layer can become inhomogeneous.

A mismatch in the sintering temperature of the particles can also lead to delamination. ALD NanoSolutions has demonstrated that $BaTiO_3$ particles can be uniformly coated with ultra-thin films to provide homogenous behaviour in thin dielectric films.

The company is also developing ALD processes suitable for the protection of the electronic displays that use electroluminescent phosphor. Currently, CVD films protect the material from moisture and oxygen but they are disordered and imperfect and the thickness of the layers required to account for the imperfections reduces the potential illuminance of the display. Although Al_2O_3 is not an effective coating material in this case because it hydrates easily, Weimer has chemistries for the deposition of titania or silica films on metal particles that could provide a thinner, more protective barrier for the luminescent material.

The potential for using organic light-emitting diodes for general lighting could be increased if the materials could be protected from degradation by water and oxygen using ALD films. ALD NanoSolutions has shown that Al_2O_3 films grown on polyethylene naphthalate substrates have the very low oxygen and water vapour transmission rates suitable for this application.

Applications for new plastics in packaging, biomedical devices, and cars are also being developed. Weimer's team has successfully deposited Al_2O_3 films on several polymer substrates. Al_2O_3 is non-flammable and has a melting point of 2050 °C so it offers a chemical and thermal stability that makes it an effective diffusion barrier. The combination of polyethylene and Al_2O_3 is also biocompatible, making it suitable for medical applications.

According to Weimer, ALD nanocomposites that can be extruded offer better manufacturing efficiency and control and fewer defects than other composites where the ceramic component may not be homogeneously dispersed within the polymer matrix at nanoscales. Weimer's team has successfully extruded micron-sized polymer particles that have been precoated by Particle ALD with a nanometre thick ceramic layer. The high shear and stress extrusion process breaks the ceramic shells which disperse to form a nanocomposite with intimately-mixed nanoscale ceramic inclusions.

ALD NanoSolutions is working on military applications including the improvement of the reactive power and reaction velocity of explosives. High energy materials used as explosives and propellants usually contain a fuel and an oxidiser.

They can be contained in the same molecule as they are in tri-nitro-toluene (TNT) or they can be mixed together as a powder composite. The reaction velocity for these powders is relatively slow as the diffusion distance between the fuel and the oxidiser is relatively large, but the energy released is great.

If the diffusion distance was reduced, much greater reactive power could be achieved. Using ALD to deposit the oxidiser directly onto the fuel particle would shorten the diffusion distance and maximise the amount of surface contact between the fuel and the oxidiser. The chemistry is still under development but SnO_2 has been grown on Al nanoparticles which, when ignited, resulted in a very rapid release of energy.

The potential of ALD technology is continually being explored and one of the most recent projects to be initiated involves coating carbon nanotubes for use in composite materials. Funded by the National Science Foundation, this project aims to improve the strength and stiffness of nanotube and ceramic composites for applications such as armour plating.

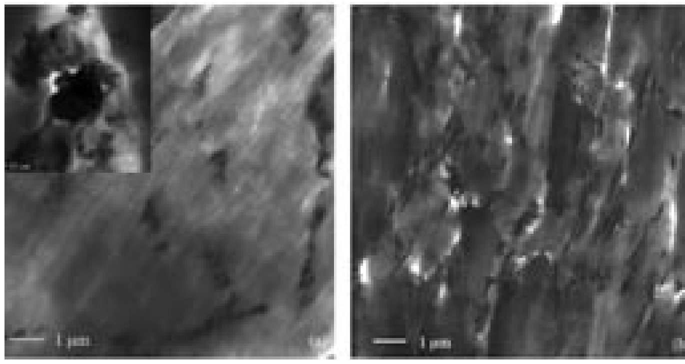
An Australian team of researchers, led by Martin Rhodes of Monash University, is collaborating with Weimer to gain a greater understanding of the fundamental properties of nanoparticles in fluidising bed reactors. Using 12 nm silica particles, they are measuring agglomerate properties and studying the effects of gas velocity on agglomerating processes.

Their efforts are directed at minimising the environmental impact of the chemical industry by the development of effective catalysts that maximise product selectivities and minimise waste.

Shan Wang of Monash University, a researcher working with Rhodes, believes that nanocatalysts have already been shown to have superior performance over conventional catalysts and fluidised bed nanoparticle reactors offer great potential for revolutionising gas-solid catalytic reaction engineering.

They can potentially reduce the mass transfer resistance for reactive intermediates and products, helping to eliminate the problems of irreducible mass transfer limitations that can occur when conventional catalysts and nanocatalysts are loaded into a porous support.

According to ALD NanoSolutions, nearly every established industry has experienced some form of critical materials problems and their platform technology offers a new generation of materials design and development possibilities. **tce**



Cross sectional TEM of HDPE/alumina nanocomposite (Left to right) (a) Extruded from 60 µm HDPE particles, (b) Extruded from 16 µm HDPE particles. The alumina shell remnants are perfectly mixed in a high density polyethylene polymer matrix, the result of extruding alumina coated polymer particles. These coatings can be placed on particles at near room temperature, allowing their coating without melting the polymer

Wendy Laursen is a freelance journalist based in Australia