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Nanoparticles

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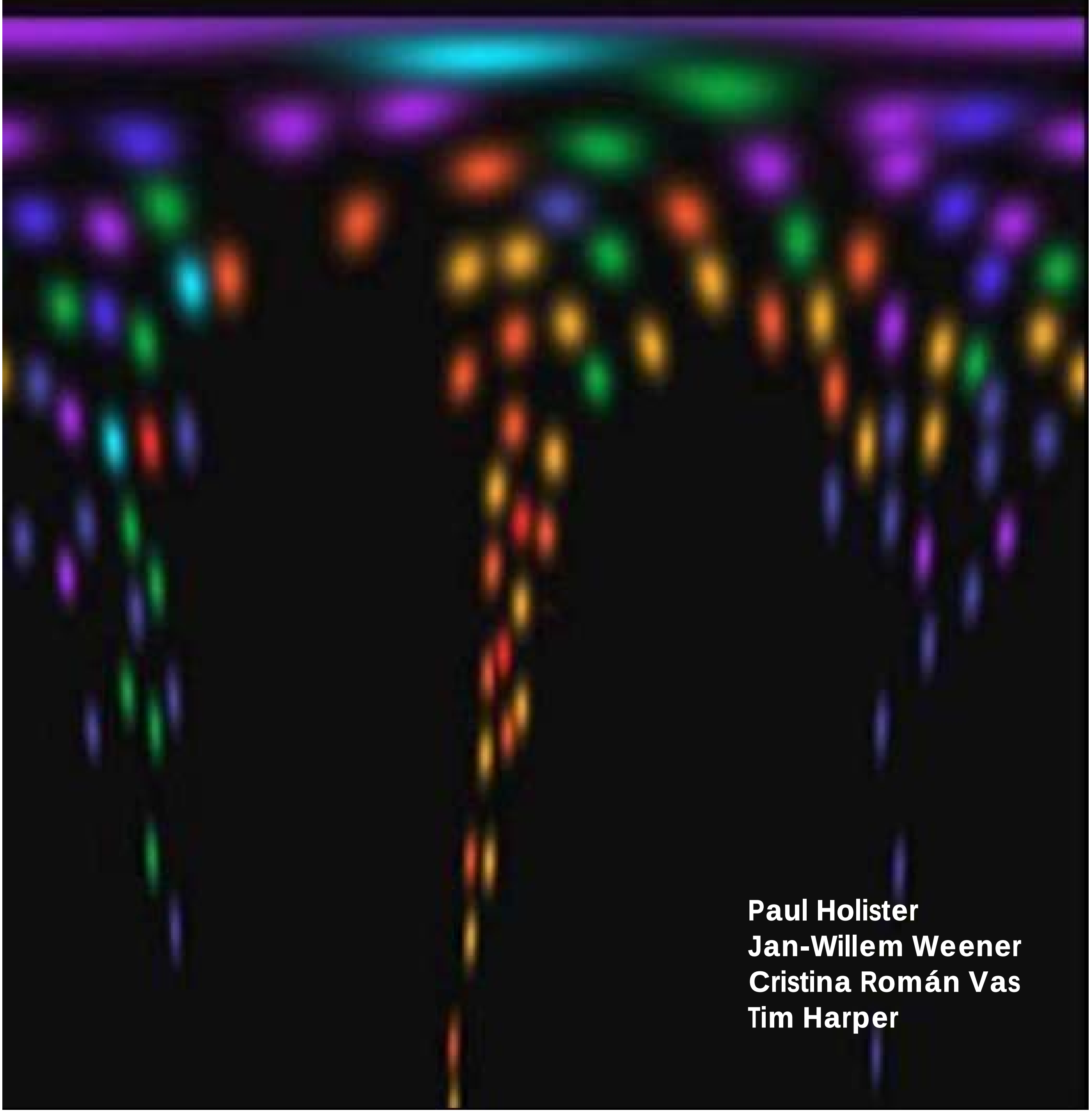
nr. 3



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Origin of content

The free reports in this series are extracted from the technology reports that make up the Nanotechnology Opportunity Report collection and are designed to offer an introduction to the variety of technologies that fall under the nanotechnology umbrella. The full reports also include 'opportunities' sections, covering the various applications of the technology and their effects on markets, and a list describing the companies involved in the technology.

Scope of this report

The term 'nanoparticle' is a very general one and is often used to cover materials that are better described using other terms. Occasionally it has been used to describe dendrimers, which are globular polymers and examples of state-of-the-art molecular engineering. This report does not include dendrimers, which are given their own report, under the term nanoparticles. Calling quantum dots nanoparticles (or nanocrystals, as is often done) is less incorrect but detracts from the fact that it is their quantum mechanical properties that are of interest rather than their nanoscale size, although the former are indeed a function of the latter. Quantum dots also deserve separate treatment and have their own report.

Nanoparticles are often crystalline and end up being referred to as nanocrystals. Such materials are included in this report but nanocrystalline bulk materials, i.e. those that contain nanoscale crystalline elements but not separate nanocrystals, are dealt with in a separate report.

Introduction to nanoparticles

Figure 1. Water droplets on a wood surface treated with BASFs "Lotus Spray". The coating combines nanoparticles with hydrophobic polymers. Courtesy of BASF, Germany.

The transition from microparticles to nanoparticles can lead to a number of changes in physical properties. Two of the major factors in this are the increase in the ratio of surface area to volume, and the size of the particle moving into the realm where quantum effects predominate.

The increase in the surface-area-to-volume ratio, which is a gradual progression as the particle gets smaller, leads to an increasing dominance of the behavior of atoms on the surface of a particle over that of those in the interior of the particle. This affects both the properties of the particle in isolation and its interaction with other materials. High surface area is a critical factor in the performance of catalysis and structures such as electrodes, allowing improvement in performance of such technologies as fuel cells and batteries. The large surface area of nanoparticles also results in a lot of interactions between the intermixed materials in nanocomposites, leading to special properties such as increased strength and/or increased chemical/heat resistance.

The transition from classical mechanics to quantum mechanics is less gradual. Once particles become small enough they start to exhibit quantum mechanical behavior. The properties of quantum dots (covered in a separate report) is a case in point. These are sometimes called artificial atoms because free electrons in them start to behave in a way similar to electrons bound by atoms in that they can only occupy certain permitted energy states.

Additionally, the fact that nanoparticles have dimensions below the critical wavelength of light renders them transparent, a property which makes them very useful for applications in packaging, cosmetics and coatings.

Some of the properties of nanoparticles might not be predicted simply by understanding the increasing influence of surface atoms or quantum effects. For example, it was recently shown that perfectly-formed silicon 'nanospheres', with diameters of between 40 and 100 nanometers, were not just harder than silicon but among the hardest materials known, falling between sapphire and diamond.

Nanoparticles have been used for a very long time, probably the earliest use being in glazes for early dynasty Chinese porcelain. A Roman cup, called the Lycurgus cup, used nanosized gold clusters to create different colors depending on whether it was illuminated from the front or the back. The cause of this effect was not, of course, known to those who exploited it.

Carbon black is the most famous example of a nanoparticulate material that has been produced in quantity for decades. Roughly 1.5 million tons of the material is produced every year. Nanotechnology, though, is about deliberately and knowingly exploiting the nanoscale nature of materials, which would, for many, exclude early use of carbon black from being given the nanotechnology label. However, new production and analysis capabilities at the nanoscale and advances in theoretical understanding of the behavior of nanomaterials certainly mean nanotechnology can be applied to the carbon black industry.

Nanoparticles are currently made out of a very wide variety of materials, the most common of the new generation of nanoparticles being ceramics, which are best split into metal oxide ceramics, such as titanium, zinc, aluminum and iron oxides, to name a prominent few, and silicate nanoparticles (silicates, or silicon oxides, are also ceramic), generally in the form of nanoscale flakes of clay. According to the most widely-accepted definitions, at least one of their dimensions must be less than 100 nm, but some interesting new applications use particles of a few hundred nanometers, so this report will not be overly strict about the 100 nm limit. The nanoparticles in metal and metal oxide ceramic nanopowders tend to be roughly the same size in all three dimensions, with dimensions ranging from two or three nanometers up to a few hundred (one might expect such fine particles to stay suspended in air but in fact they settle out into a very fine powder, drawn together by electrostatic forces).

Silicate nanoparticles currently in use are flakes about 1 nm thick and 100 to 1000 nm across. They have been produced for many years now, the most common type of clay used being montmorillonite, a layered alumino-silicate. The nanoparticles can be incorporated in a polymer either during polymerization or by melt compounding (mixing in with a plastic 'melt'—for thermoset plastics this is a one-time process since they become set by heat, and cannot be re-melted. Thermoplastics, by contrast, can be repeatedly softened by heating).

Pure metal nanoparticles can be induced to merge into a solid, without melting (a process called sintering) at lower temperatures than for larger particles, leading to improved and easier-to-create coatings, particularly in electronics applications such as capacitors. Metal oxide ceramic nanoparticles can also be used to create thin layers, whether crystalline or amorphous.

Ceramic nanoparticles, like metallic nanoparticles, can also be formed into coatings and bulk materials at lower temperatures than their non-nano counterparts, reducing manufacturing costs. Superconducting wires have been made out of ceramic nanoparticles, creating a material that is relatively flexible where traditional ceramic materials are far too brittle. A very active area of research and development on nanoparticles surrounds their use to make nanocrystalline coatings, the novel properties of which are covered in a separate report. Nanocrystalline ceramics are already in use, by the US Navy, for example.

Although metal oxide ceramic, metal, and silicate nanoparticles constitute the majority of nanoparticles with current and expected applications, there are others too. A substance called chitosan, used in hair conditioners and skin creams, has been made in nanoparticle form and the process was patented late in 2001. These nanoparticles improve absorption.

Production techniques

There is a wide variety of techniques for producing nanoparticles. These essentially fall into three categories: condensation from a vapor, chemical synthesis, and solid-state processes such as milling. Particles can then be coated, with hydrophilic (water-loving) or hydrophobic (water-hating) substances, for example, depending on the desired application.

Vapor condensation

This approach is used to make metallic and metal oxide ceramic nanoparticles. It involves evaporation of a solid metal followed by rapid condensation to form nanosized clusters that settle in the form of a powder. Various approaches to vaporizing the metal can be used and variation of the medium into which the vapor is released affects the nature and size of the particles. Inert gases are used to avoid oxidation when creating metal nanoparticles, whereas a reactive oxygen atmosphere is used to produce metal oxide ceramic nanoparticles. The main advantage of this approach is low contamination levels. Final particle size is controlled by variation of parameters such as temperature, gas environment and evaporation rate.

A technique that is arguably not really vapor condensation is the "exploding wire" technique, developed originally in Russia and currently used by Argonide. An electrical arc is created at the surface of a metal wire with sufficient energy to explode or vaporize clusters of atoms (similar to blowing a filament in a light bulb). These clusters then condense within an inert gas into nanoscale particles.

Another variation on the vapor condensation technique is the vacuum evaporation on running liquids (VERL) method. This uses a thin film of a relatively viscous material, an oil, or a polymer, for instance, on a rotating drum. A vacuum is maintained in the apparatus and the desired metal is evaporated or sputtered into the vacuum. Particles form in suspension in the liquid and can be grown to a variety of sizes.

Toshiba has developed a new nanoparticle production method based on the chemical vapor deposition (CVD) technique generally used to make thin films for use in large-scale integrated circuits. Both liquid and gas forms of a substance are put into a reactor. Depending on several parameters (like gas-to-liquid ratio, the order in which the gas and liquid are added, the temperature and length of time during which heat is applied), different particle shapes can be created and controlled (homogeneous nanoparticles can be important in many applications—nanoparticles used in a magnetic disk to record data, for example, must all be much the same size). The company tested the process using titanium oxide and managed to make spheres measuring 1-100 nanometers in diameter, as well as a nucleus covered with many particles or clusters of particles.

Chemical synthesis

The most widely used chemical synthesis technique consists essentially of growing nanoparticles in a liquid medium composed of various reactants. This is typified by the sol–gel approach and is also used to create quantum dots (nanoparticles in which quantum mechanical properties are the key to their useful behavior). Chemical techniques are generally better than vapor condensation techniques for controlling the final shape of the particles. The ultimate size of nanoparticles might be dictated, as with vapor condensation approaches, by stopping the process when the desired size is reached, or by choosing chemicals that form particles that are stable, and stop growing, at a certain size. The approaches are generally low-cost and high-volume but contamination from the precursor chemicals can be a problem. This can interfere with one of the common uses of nanoparticles, sintering, to create surface coatings.

Solid-state processes

Grinding or milling can be used to create nanoparticles. The milling material, milling time and atmospheric medium affect resultant nanoparticle properties. The approach can be used to produce nanoparticles from materials that don't readily lend themselves to the two previous techniques. Contamination from the milling material can be an issue.

Developments in production techniques

As the market for nanoparticles in high-tech areas, such as the computer and pharmaceutical industry, continues to expand, the demand for nanoparticles with a well-defined size and/or shape in high volumes and at low cost continues to increase. This trend is responsible for a continuous refinement of existing manufacturing technologies and for the development of novel production techniques.

In the past two years researchers have begun to use supercritical fluids (SCFs) as a medium for metal nanoparticle growth. Supercritical fluid precipitation processes can produce a narrow particle size distribution. A gas becomes a supercritical fluid above a critical point, at a certain temperature (critical temperature, T_c) and pressure (critical pressure, P_c). SCFs possess properties that are intermediate between liquids and gases. Generally CO_2 is used because of its relatively mild supercritical conditions (T_c = 31°C, P_c = 73 bar). Moreover, it is inexpensive, non-toxic, non-corrosive and not explosive or flammable. A possible refinement of the supercritical fluid technology involves the stirring of surfactants (see glossary) with an aqueous metal salt solution in supercritical CO_2. This process leads to the formation of microemulsions, which can be viewed as potential nanoreactors for synthesizing extremely homogeneous nanoparticles.

Sumitomo Electric has recently developed an electrodeposition process in which metallic ions are dissolved in an aqueous solvent, which is subsequently reduced to produce metallic nanoparticles at. The company claims that the process is very cost competitive when compared with chemical vapor deposition approaches.

Other novel production techniques have been reported based on the use of microwaves, ultrasound, and biomimetics (mimicking biology).

Biological processes are worth keeping an eye on because of the ability of natural systems to create almost atomically perfect nanostructures. Some bacteria create magnetic or silver nanoparticles, and bacterial proteins have been used to grow magnetite in laboratories. Yeast cells can create cadmium sulfide nanoparticles. More recently, researchers in India found a fungus capable of making gold nanoparticles, while others in the US used viral proteins to create silver nanoparticles with interesting and well-formed shapes. There is a continuum between biomimetic approaches and chemical synthesis with the use of macromolecules such as dendrimers sitting close to the middle. These have been used to make amorphous calcium carbonate nanoparticles (this being a material that biological systems are particularly adept at using).

Coating and chemical modification of nanoparticles

Coating or chemically modifying a variety of nanoparticles is common practice and an area where new, valuable, innovations are likely to be seen.

Silicate nanoparticles are hydrophilic (water-loving) and need to be chemically modified to make them more hydrophobic (water-repellent), for example with larger molecules such as polyhedral oligomeric silsesquioxanes (POSS—see glossary), which are popular both for coating silicate nanoparticles and as a filler for composites on their own. The customizable side groups on POSS can assist in making polymers easier to graft to each other and hold promise for initiating protein adhesion in biomaterials. At about 1.5 nm in radius, POSS are themselves sometimes classified as nanoparticles.

Ferrofluids, made since the early 1960s, use magnetic nanoparticles as small as 10 nm across that are coated with a stabilizing material, graphite being one example, and suspended in a carrier such as oil, water, or kerosene. Each particle is a little magnet and applying a magnetic field aligns the particles, creating unusual fluid behavior and allowing magnetic control of pressure, viscosity, electrical conductivity, thermal conductivity, and optical transmissivity of the fluid. The fluids absorb energy when subjected to a magnetic field. The absorbed energy is taken from the environment in the form of heat and thus these fluids can be used as refrigerants.

Glossary

Biomimetics

The development of a novel material/product based on an idea, principle or mechanism borrowed from nature.

Catalyst

A substance that alters the rate of a chemical reaction and may be recovered essentially unaltered in form and amount at the end of the reaction.

Graphite

Material that consists of planes of hexagonal arrays of carbon atoms.

Hydrophilic

A compound is hydrophilic (water-loving) when it mixes with water.

Hydrophobic

A compound is hydrophobic (water-repelling) when it is immiscible with water. Oil is hydrophobic.

High-Barrier Plastics

Plastics which, normally through the incorporation of silicate nanoparticles, display reduced gas permeability. This effect stems from the flake shape of the nanoparticles, which forces molecules to travel a long path through the material.

MRI

Molecular Resonance Imaging. Medical imaging technique.

Paclitaxel

Paclitaxel is the active ingredient in Taxol, the world's most used cancer-fighting agent.

POSS

Polyhedral oligomeric silsesquioxanes. POSS consist of an inorganic (silicon–oxygen) core and eight variable organic side groups and are typically about 1.5 nm in radius.

Supercritical Fluid (SCF)

Supercritical fluids possess properties that are intermediate between gases and liquids. A gas becomes a supercritical fluid above a critical temperature (Tc) and a critical pressure(Pc).

Surfactant

A surface-active substance, such as a detergent or soap, that lowers the surface tension of a solvent (usually water).