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Nanoforum Report:

Nanotechnology in Consumer Products

October 2006

Nanotechnology in Consumer Products

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1. Introduction

More and more consumer products are branded with the buzzword “nano” or nanotechnology. Are we witnessing the onset of an emerging technology or is it just a sophisticated advertisement strategy? If the technology is true, what is the added value to certain products and does the consumer really benefit? In general the products claiming to contain nanotechnology do indeed exploit nanoscale effects, primarily interface effects but also a few quantum effects. Interestingly, the products that proudly use the “nano” brand are only a small percentage of the number of consumer products that actually contain nanotechnologies, for instance in the microelectronics, cosmetics, pharmaceutical and food industries. The following report focuses on consumer products emerging in various commercial sectors which claim to have nanotechnological products on the European market.

The field of nanotechnology is vast and interdisciplinary, ranging from medicine and healthcare to construction and consumer electronics. For this reason the definition of “nano” may vary and even among experts no consensus can be found today. The weakest definition of nanotechnology claims the ability to control matter at a level below 100 nm. A more demanding definition requires that new effects or functions have to play a critical role. Structures at the atomic and molecular scale obey rules that strongly differ from those in our macroscopic world, such as quantum effects which give rise to new applications.
The following definition is applied for this report:
“Nanotechnology is the exploitation of the ability to control matter at dimensions between 0.1 and 100 nm, resulting in unique functionalities.”
Besides serious science, nano has also become a buzzword, a gadget which is nice to have. Today “nano” is also used as a synonym for “new” and “innovative”. Therefore existing technologies are sometimes simply renamed to fulfil modern requirements. A major drawback is the current lack of standardization which would be helpful to distinguish between commercializing strategies and technology. Hence, it is not astounding that the number of nanotechnology patents worldwide has increased exponentially.

2. Effects and Innovations

General considerations

The vast majority of nanotech consumer products on the market today make use of interface effects. The interface is a two dimensional surface that marks the boundary between two materials. When an interface is made rougher, for instance, this surface area increases. Likewise, when particles are made smaller the surface area to volume ratio increases. A material consisting of nanoscopic building blocks exhibits an extremely large surface area to volume ratio. This effect influences for example the catalytic activity of nanoparticles. The inverse, a nanoporous structure, can be used as membrane in filtration processes or as an insulation material (e.g. zeolithes). This effect can also be exploited when a property of a given material is applied to a surface (e.g. scratch resistance). In many cases, a tiny, almost invisible coating of the material will still provide the desired physical property.

Another class of effects that is beginning to be incorporated into nanotech products are quantum mechanical effects, albeit to a much lesser degree than interface effects. Quantum mechanics can result in unique optical, electrical and magnetic properties of nanomaterials. This effect was exploited as early as medieval times when gold nanoparticles were used to endow church windows with a reddish color. A modern mp3 player stores data in a flash memory using the quantum mechanical tunneling effect.

Finally, although it is not a typical physical effect as in the case of interface and quantum effects, complexity is another important factor leading to added value in nanotech consumer products. The consumer benefits from the integration of smaller and smaller devices have been most clearly illustrated by the microelectronics industry. There appears to be no end in sight to the steady improvement of processor speed and memory density by using miniaturization to create more complex circuitry.

Several product innovations rely either on the use of nanoparticles or so called nanotubes (fullerenes). Many other products deal with improved water repellency. For this reason these three issues are briefly introduced below. This is followed by a comprehensive list of effects and innovations.

Fullerenes

Fullerenes are an allotrope of carbon, similar to the better known allotropes graphite and diamond, but with nanoscopic shapes ranging from spherical to cylindrical. The first fullerene to be discovered was C_{60}, consisting of 60 carbon atoms arranged in 12 pentagons and 20 hexagons (identical in shape to that of a soccer football). This molecule was named Buckminsterfullerene, after the architect Richard Buckminster Fuller (1895-1983), as the molecules share the architecture of his geodesic domes. Soon after the discovery of this molecule other variations on the structure were discovered and these are collectively referred to as fullerenes.

Fullerenes can also be shaped as cylindrical nanotubes. The most common form of nanotube is the carbon nanotube (CNT), although nanotubes can be formed from other elements as well. Nanotubes may occur individually as single-walled carbon nanotubes (SWNT) or stacked concentrically one into another, as multi-walled carbon nanotubes (MWNT). Nanotubes have attracted increasing attention due to their unique physical properties. They are capable of carrying an extremely high electrical current and are very good thermal conductors. Another unique property is their unusually high tensile strength which could be as large as 300 GPa in theory[1] (steel is ~ 1-2 GPa). For this reason CNT have the potential to improve mechanical properties e.g. of polymers. In this sense, the following parameters play a critical role in order to enhance the material strength:

- the connection of the nanotubes to the polymer matrix. This parameter can be influenced by adding functional groups to the CNT surface to establish covalent bonds to the matrix. CNTs with different chemical functional groups are available.
- the length of the individual tubes (aspect ratio). Stronger material can be obtained with longer tubes.
- exfoliation. Nanotubes tend to occur in bundles after production. These bundles have to be fully exfoliated to obtain individual tubes.

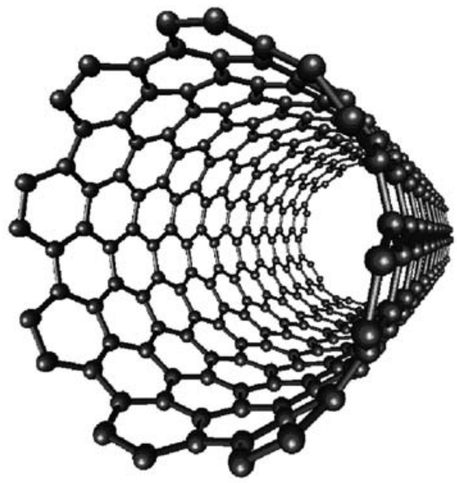

Figure 1: A single-walled carbon nanotube (SWNT) can be thought of being a rolled-up sheet of graphite. The diameter and the length of the nanotubes may vary. Infineon AG

[1] Min-Feng Yu, Oleg Lourie, Mark J. Dyer, Katerina Moloni, Thomas F. Kelly, Rodney S. Ruoff, **Strength and Breaking Mechanism of Multiwalled Carbon Nanotubes Under Tensile Load,** *Science*, 287 (2000) 637.

- dispersion. The nanotubes have to be fully dispersed within the polymer matrix to obtain a homogenous material with optimum strength.

However, a broad use of such nanotubes is limited today by their comparatively high price. There is also a problem in uniformity, regarding the diameter, length and electrical conductivity. Although progress has been made in this direction, producing large quantities of pure metallic or pure semiconducting carbon nanotubes with a specific diameter and length is still too prohibitively expensive.

Nanoparticles

When particles of a material are made smaller their surface area to volume ratio increases. The most obvious advantage of this is in cases where a large surface of a valuable material is necessary, for instance in the use of platinum nanoparticles in catalytic converters. However, another benefit is that cheaper materials can become valuable just because they are in nanoparticlulate form. This can occur because when the particle is small enough (e.g. below ~100nm), the properties of this interface can become more important than the properties of the material itself. As a result, only a tiny amount of this nanomaterial is needed to add new properties to a product. For example the hardness of silicon dioxide (SiO_2, glass) can be used to lower the wear and tear of scratch sensitive surfaces by incorporating SiO_2 nanoparticles. This even works on flexible surfaces such as textiles, since the nanoparticles do not exhibit the undesired brittleness of the macroscopic glassy solid.

Numerous product innovations rely on the incorporation of nanoparticles in an organic matrix, often referred to as nanocomposites. Ultrafine carbon particles, called carbon black are widely used as a reinforcing filler material in rubber products such as automobile tyres and as a pigment in printer toner.

Figure 2: Modern tyres consist of the tread, the steel cord belt and the nylon cord carcass (left). Aggregates of carbon black particles dispersed in rubber matrix are used for reinforcement (right). Degussa AG

In addition to changes in mechanical properties, a variety of other properties of materials can change when the material is in nanoparticle form – including mechanical, solubility, magnetic, electrical and more. Of particular interest is the incorporation of zinc oxide (ZnO) or titanium dioxide (TiO_2) nanoparticles into sunscreen. These are effective UV absorbers and have been used for decades in sunscreens. However as large (microscopic) particles these materials appear as white pastes which limits their aesthetic appeal. By making the particles smaller they no longer absorb visible light, and therefore the sunscreen appears transparent, while still absorbing dangerous UV light from the sun.

As particles become even smaller (e.g. below 10nm), energy levels become quantized which means that the particles behave more like atoms or molecules than classical particles. Such nanoparticles are typically referred to as quantum dots. For example, the colour of macroscopic gold is yellow. However, gold nanoparticles in solution are red, due to surface plasmon excitation. Although quantum dots are primarily used in medical diagnostics and biotech industries for molecular recognition, they are beginning making an appearance in consumer products, for instance in laser diodes and home pregnancy tests.

The wetting of surfaces

Wetting phenomena are playing a dominant role in different surface treatment strategies, as described below. The wetting of a surface is determined by the interfacial tensions of the wetting liquid, the wetted solid and the surrounding gas phase. Besides these three parameters, which are caused by molecular interactions, the surface roughness or specific structures play a key role in wetting phenomena.
Surfaces can be divided into hydrophobic (water hating) and hydrophilic (water loving) surfaces. Well known hydrophobic surfaces are all kinds of plastics, especially those with a large proportion of fluorinated carbons, such as Teflon. Prominent hydrophilic surfaces are all untreated metals and glass surfaces. From a chemical point of view, surfaces can be classified as reactive or inert, where a hydrophilic surface typically has a much stronger affinity to bind adsorbates and a hydrophobic surface has not. Unfortunately, many technically relevant materials fall within the reactive species, such as metals and glass. Such surfaces tend to stain easily due to their high surface

Figure 3: A hydrophobic wooden surface. BASF AG

energy. A clean metal can easily reach several 1000 mN/m (iron is ~ 2500 mN/m), depending on its cleanliness. In contrast Teflon has a surface energy of just 18 mN/m. For this reason several attempts have been made to reduce the interfacial tension of technical relevant surfaces.

The wetting condition of a surface is defined by the contact angle, which is the slope of the tangent at the intersection of solid and liquid.
A contact angle of 0° corresponds to complete wetting. In the case of water, this phenomenon is often termed super-hydrophilicity or complete wetting. At the other extreme is a contact angle of 180°. Surfaces with very large contact angles are called super-hydrophobic. A surface with a contact angle of 180°, for example, has been achieved by a vertically grown Teflon coated nanotube forest[2].

Effects and corresponding innovations

The different effects described above can be used to overcome several drawbacks in consumer products that are currently available on the market. Many different terminologies have been defined to address the various drawbacks or to describe innovations. The following list provides an outline of existing terms complete with a short description of the technology:

a) Interface Effects

So far most nanotechnology-related products exploit this effect. This approach typically offers advanced material properties by adding nanoscopic particles either in the bulk material or on the surface. Physical properties, such as electrical and thermal conductivity, or mechanical strength, can be changed significantly when the bulk composition is altered. Other properties can be appropriately addressed by modifying the surface composition. These include scratch resistance, water repellency, reflectivity and photo activity to name but a few. Such novel materials are frequently correlated to either nanoparticles or nanotubes. Both of these are briefly addressed below.

Lotus-Effect

The leaves of the Lotus plant exhibit an extremely high water and oil repellency which is based on hydrophobic wax crystals in combination with a micro- and nanosized surface roughness. It is a combination of structure and chemistry that defines the lotus surface unique properties.

[2]Lau, K.S.K.; Bico, J; Teo, K.; Chhowalla, M.; Milne, W.; McKinley, G.H.; Gleason, K. K. **Superhydrophobic Carbon Nanotube Forests**, *Nano Lett.*, **3**(12), (2003), 1701-1705.
http://web.mit.edu/nnf/publications/GHM72.pdf

Even very sticky and highly viscous liquids such as honey or glue roll off when the surface of the leaf is slightly tilted. However, the tiny structures on the surface can be easily disturbed which is disadvantageous for most technological applications. For this reason a synthetic lotus effect is hard to achieve on technical surfaces, especially when mechanical stress is involved.
Furthermore, the natural structures of a lotus leaf are bigger than the 100 nm. Since nature has evolved its "products" very well, one could argue that nanotechnology is not needed to mimic this effect.
Nevertheless, in order to distinguish between a surface with a lotus effect and other hydrophobic surfaces the following requirements have to be met[3]:
1) The static contact angle against water has to be at least 140° measured for a 20 µl droplet after 1 min time of relaxation.
2) The hysteresis between the advancing and receding contact angle is not larger than 10°.
3) The minimum tilt angle of the surface, where a 20 µl droplet applied from a height of 1 cm height rolls off, is 10°.
4) A sample tilted by 10° shows no wetting water film after 30 min of continuous standardized showering.

Easy-to-Clean

The problem of surface contamination is widespread, especially when considering high energy surfaces such as glass or metal, which have a strong tendency to adsorb other molecules. Common strategies are based on the reduction in the surface free energy without losing the material properties, e.g. transparency. Generally the water and oil repellency is increased when the contact angle of water is above 100°. This phenomenon is exploited in non-stick surfaces such as frying pans (Teflon). New approaches are based on organic/inorganic nanocomposites which provide properties similar to perfluorinated polymers such as Teflon.

Anti-Graffiti

The major drawback of common plaster, bricks or concrete is its strong absorbency which provides an excellent substrate for long-lived graffiti. A common approach to overcome this is based on a poly-urethane (PUR) coating that provides a permanent protection and stops the paint from permeating into the wall. This can consist of a two component system, which reacts after application directly on the wall. Any graffiti on the protected surface can be removed easily. However, there is little in this coating that is really "nano", although this term is sometimes mentioned in this field.

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[3] Deutsche Bundesstiftung Umwelt, www.dbu.de

Antimicrobial Coating

Fighting bacteria and other microbes is commonly achieved by certain chemical agents. Two inorganic approaches can be used for sanitizing surfaces. The first is based on the photocatalytic activity of titanium dioxide as described below. The second exploits the toxicity of certain metallic cations such as silver. Silver has long been known for its excellent antimicrobial effect due to the release of silver ions which are taken up by microbes and exert a toxic effect. Modern approaches increase its activity by dispersing silver in ultra fine particles. The extreme increase in surface area enhances silvers natural sanitizing ability.

Anti-fingerprint

Metallic surfaces such as stainless steel get easily stained when touched with bare hands. The optical reflectivity of the material changes due to the transfer of grease from the skin. Although the deposition of finger grease cannot be prevented entirely, an anti-fingerprint coating reduces the visibility by camouflaging their traces. The refractive index of the protective coating matches that of the grease. Therefore, anti-fingerprints coated metal surfaces appear darker compared to their unprotected counterparts.

Antifog

Bringing a cold surface into a warmer surrounding will lead to fogging. This effect is inevitable unless the surface is heated. It results from the formation of tiny droplets on the mirrors surface scattering the light and nebulizing reflections. A superhydrophilic coating can prevent droplet formation to a certain extent. The droplets simply merge into a thin water layer on the mirror without changing the reflectivity too much.

Photocatalytic TiO_2 coatings are super-hydrophilic when exposed to sufficient UV light.

Corrosion protection

Steel parts in automotive manufacture are commonly heat-treated to achieve the desired shape. During this heating process (of up to 1000 degrees centigrade) the steel will corrode. It can be protected against high temperature corrosion (scaling) by applying a nanoparticulate coating.

Wear and tear protection

A reduction of wear and tear on surfaces in mechanical contacts can be achieved either by decreasing friction or by stiffening surfaces through coatings. The friction coefficient can be reduced by diamond-like carbon coatings (DLC). These amorphous coatings offer a hardness of around 20 GPa. Another approach is based on surface textures which reduce the friction efficiently.

Scratch resistance

Hard nanoparticles, such as silicon dioxide, can be used to build up scratch resistant coatings. For example, they can be incorporated in an organic matrix to improve the scratch resistance of lacquers.

Diffusion barriers

Certain beverages, such as beer, were not available in PET bottles for a long time. The strong oxygen permeability of such plastic bottles contributed to a short shelf-life. Layered silica (SiOx) can reduce oxygen permeability effectively. The thickness of this glassy SiOx coating ranges from 50 to several hundred nanometres. The material is a mixture of SiO_2 and SiO and therefore denoted by SiOx with x being between one and two. The same material can also be used for packaging foils.

Tensile strength / Impact strength

Adding nanoscale components into composites will enhance their tensile and impact strength. Carbon nanotubes offer the highest tensile strength ever observed. In this sense, carbon nanotubes are expected to be of great importance in the future.

Flame retardancy

Nano additives such as nanoparticles have been proven to work as flame retardants in polymers or to improve the function of existing flame retardants. The nanocomposite will influence the crust formation and works as a barrier for pyrolysis gases. Both are critical factors for fire extinction. In addition, it inhibits the dripping of burning polymers.

Fire protection

Fire-resistant windows have a transparent gel between the sheets of glass. In the event of a fire, the gel starts to swell forming a mechanically stable, opaque foam. Dispersed silica nanoparticles may improve the durability of the fire-protection.

Lightweight construction

Reducing the weight of a material, but maintaining its mechanical strength is a common objective in designing novel materials. In this sense, magnesium alloys are promising candidates. Another approach is based on reinforced polymers using carbon fibers.
Ultimately, the use of nanofibers, such as carbon nanotubes, may replace existing technologies.

Insulation

The principle of insulating material is based on high porosity which encloses as much air as possible. The material exploits the low thermal conductivity of air, and free air flow is inhibited. Thus the density of such a material is an important measure. The lower the density the more air is enclosed and the better the insulation will be. The insulating ability of a given material, e.g. glass wool, can be increased by thickening the insulating layer.
In this regard, nanoporous materials offer superior properties. Silica aerogels have the lowest thermal conductivity and density of all solids. They are sometimes called frozen smoke. Their thermal conductivity can be as low as 0.016 W/(m·K)4, with a density of 0.005-0.2 g/cm^3. They are manufactured through a sol-gel process. Nevertheless, a silica aerogel is very brittle and expensive to produce. Therefore, flexible and cheaper alternatives have been produced, which offer a superior insulation and can be much thinner than traditional insulating material.

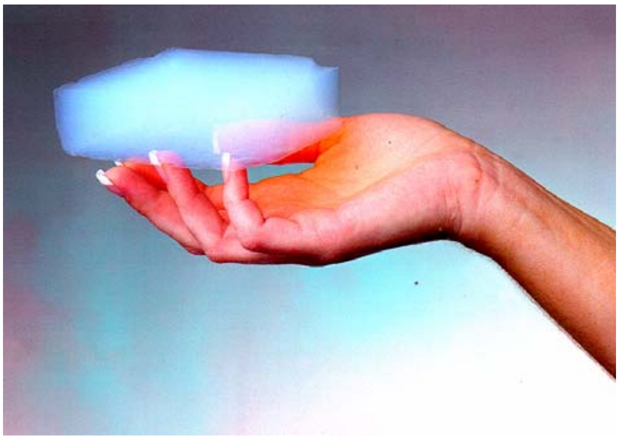

Figure 4: A silica aerogel is virtually made of air (up to 99, 5 %), Source NASA.

[4] http://stardust.jpl.nasa.gov/aerogel_factsheet.pdf

Bond and disbond on command

Gluing has become more and more important in many production processes. Heat is often applied to harden the glue. This process can be accelerated significantly by dispersing magnetic nanoparticles within the glue. Applying an external electromagnetic field "shakes" the nanoparticles, causing them to heat up and thus heat up the glue very locally. This effect is called "bonding on command" and saves both energy and time. Furthermore it can be applied to buried interfaces very efficiently. The process offers also a non-destructive method to separate glued surfaces by irradiation (disbond on command).

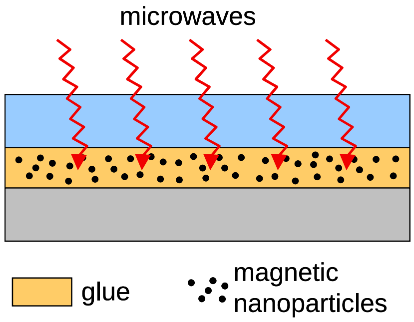

Figure 5: A glue containing magnetic nanoparticles can be heated up selectively by microwave irradiation. VDI TZ

Self-cleaning surfaces/ Photocatalytic surfaces

Ultra hydrophobic surfaces or Lotus-effect surfaces are contaminated to a far lesser degree than surfaces with a higher interfacial tension. In addition, loosely bonded dirt particles are removed easily by wetting e. g. during a rain fall. Besides this strategy to increase the intrinsic stain repellency of a surface by reducing its free energy, one can directly attack adsorbants by decomposing them through photocatalysis. Thus even a highly sticky surface, such as glass, could be equipped with a self-cleaning finish which is activated with UV light. However, this approach is only suitable for outdoor applications (e.g. facades).
A common material for photocatalytic coatings is titanium dioxide (TiO_2). TiO_2 is a non-specific light scatterer and a UV absorber. The first property makes it a perfect ingredient for white paint (white pigment), the latter provides the self-cleaning and UV-protection ability.
TiO_2 is a compound semiconductor which exists in three different chemical forms: anatase, rutile and brookite type, and only the first two are widely used for different applications.
Although the band gap of anatase is slightly larger than that of the rutile type (3.2 eV compared to 3.0 eV), its photocatalytic activity is higher. For this reason anatase is commonly used as photocatalyst, and the rutile type is used as a standard white pigment.

The photocalalytic activity is based on the absorption of UV light above the band gap of 3.2 eV corresponding to a wavelength of 388 nm. Electrons jump into the conduction band leaving a hole in the valence band. In a non-photocatalytic material the charge carrier will recombine quickly. However, if the time of recombination is long enough, electrons and holes may induce the formation of free radicals. Holes act as an oxidant and electrons as a reducer. Water molecules at the surface of the anatase particle will decompose forming hydroxyl (OH^-) anions which have a high oxidation potential. These free radicals cause the decomposition of organic molecules which results in the desired self-cleaning effect.

The photocatalytic activity can be enhanced by lowering the recombination rate of electrons and holes in anatase TiO_2 particles. This can be achieved by doping the particles with silver[5]. The presence of silver gives an additional antibacterial property as previously described.

UV protection

Dispersed TiO_2 and ZnO particles are excellent UV filters, and are sometimes referred to as mineral or physical filters. In contrast, most sunscreen formulations contain classical chemical filters, based on the ability of complex molecules to absorb in the UV range. Both TiO_2 and ZnO are commonly used as white pigments (titanium white and zinc white). TiO_2 in the rutile form is the most common white pigment due to its extremely high refractive index (n=2.8). Ultrafine TiO_2 and ZnO particles lose their capability to scatter visible light, but retain the ability to absorb UV light. The bandgap of ZnO (3.2 eV) is similar to that of TiO_2 in the anatase modification and a little larger than the rutile type. When using TiO_2 for UV protection the rutile type is more suitable due to its lower photocatalytic activity, which could destroy the surrounding matrix. Mixed material containing both forms (anatase/rutile) is also in use.

The undesired photocatalytic activity can be significantly reduced by doping TiO_2 crystals with manganese[6].

One problem of ultra fine particles is their tendency to form agglomerates resulting in poor dispersion within the carrier matrix. This drawback can be overcome by coating the particle's surface, e.g. silica-coated ZnO particles.

Anti reflective coating / Moth-eye structure

In many applications a strong reflection from a smooth surface is undesirable, e.g. for displays or spectacles. The reflectivity of a surface can be reduced by two different concepts: the first introduces a micro- and nano-roughness, which

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[5] **Titanium-Oxide Photocatalyst**, Three Bond Technical News, Jan 1 2004, http://www.threebond.co.jp/en/technical/technicalnews/pdf/tech62.pdf

[6] Wakefield, G., Lipscomb, S., Holland, E.; Knowland, J. **The effect of manganese doping on UVA absorbtion and free radical generation of micronised titanium dioxide and its consequences for the photostability of UVA absorbing organic sunscreen components**, *Photochem. Photobiol. Sci*., 3 (2004) 648-652.

reduces uniform reflection through light scattering. This concept is sometimes referred to as nano-moth eye structure because the same principle is found in the facet eyes of insects and acts as part of their camouflage. It can also be used to increase the sensitivity of solar cells due to the enhanced transmission. Nevertheless, the size of an efficient moth-eye structure has to be in the range of 200 nm. The easiest way to obtain such a structure is embossing, which is limited to comparatively small areas.

The second concept is based on a coating of alternating layers of silicon dioxide and titanium dioxide. These two materials provide a strong contrast in refractive index resulting in a significantly higher transmission and reduced reflection. Although being more expensive, the second concept offers a better control. However, the thickness of the layers is in the range of several hundred nanometers and thus not truly a subject of nanotechnology.

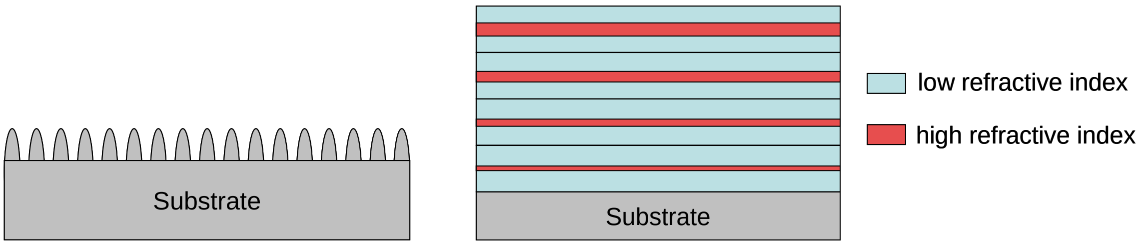

Figure 6: Comparison between a moth-eye structured surface (left) and an antireflective coating (right). Both methods reduce the reflection efficiently.

Iridescent colors / photonic crystals

Regular structures exhibiting a pitch of several hundred nanometres interact strongly with light. This is termed structural colour and is used by nature to achieve iridescent colours. The wings of some butterflies have a regular pattern of holes as revealed in Figure 7 under the electron microscope. Another example is nacre, or mother of pearl, which is a layered structure made up of hexagonal platelets. Finally, precious opals are famous for their iridescent colour. Here, silica spheres are arranged in a regular pattern which provides the base for complex light interference. The latter example is of relevance, as such inverted structures are under investigation for different electro-optical applications. Photonic crystals are essentially manmade inverted opals. However, all three examples make use of structures and periodicities from 100 to 500 nm.

Figure 7: The iridescent colours of distinct butterfly wings (left: BASF) are caused by a structured surface and contain no dye as revealed in the electron microscopic image (right: MicroAngela, http://www.pbrc.hawaii.edu/microangela).

Sealing / damping

Magnetizing a fluid is impossible, but magnetic nanoparticles can be dispersed in a suitable solvent resulting in a magnetic suspension which is sometimes referred to as a ferrofluid. Precipitation of nanoparticles can be prevented by making the particles small enough (10-30 nm). In this size range thermal excitation of the particles is sufficient to maintain a stable solution. Coated magnetite (Fe_3O_4) nanoparticles provide a super-paramagnetic liquid. Ferrofluids are already in use in alterable shock absorbers, speakers and rotary ducts. A ferrofluid shows characteristic spikes when brought into an external magnetic field as shown in Figure 8 (Rosensweig instability).

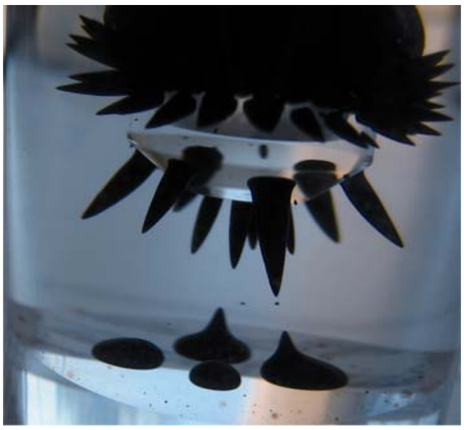

Figure 8: A magnetic liquid, termed a Ferrofluid, is a stable supension of magnetic particles in a solvent. VDI Technologiezentrum GmbH.

Dynamic viscosity / Thixotropy

Nanoparticles and other additives are also used to influence the viscosity or thickness of liquids. For some applications, such as painting, a lower viscosity is desired when the material is applied, but it should thicken quickly following this. This dynamic viscosity is referred to as thixotropy and can be found in non-Newtonian fluids. Paint for example should be easy to apply but surface sagging should be prevented. Different properties of fluids can be addressed by adding a so-called rheology modifier which is also widely used in food.

b) Quantum-mechanical effects

Tunneling Effect

The tunneling effect occurs when a small particle penetrates a barrier by using a classically forbidden energy state. This quantum mechanical effect is based on the fact that particles, e.g. electrons, have to be regarded more as a wave than a small hard sphere. By making use of the tunneling effect, an electric current will flow through a thin isolating barrier when a voltage is applied. This effect is used in flash memories to store electrons on an electrically isolated gate and in tunneling magneto resistance (TMR) elements to separate adjacent ferromagnetic layers.

GMR and TMR Effect

The giant magneto resistance (GMR) effect is based on the spin dependent scattering of electrons through a stack of ferromagnetic layers. Two thin ferromagnetic layers are separated by a conducting, but non-magnetic spacer. Their relative orientation to each other can be parallel or anti-parallel (coupling). When the orientation is parallel, the spin dependent scattering of electrons is minimal and a current flowing through the stack of layers has the lowest resistance. In the case of the anti-parallel orientation, the scattering and thus the electrical resistance is maximized (Figure 9).
This effect is widely used in read-and-write heads of hard disk drives. The read-and-write head scans data on the surface at a distance of several tens of

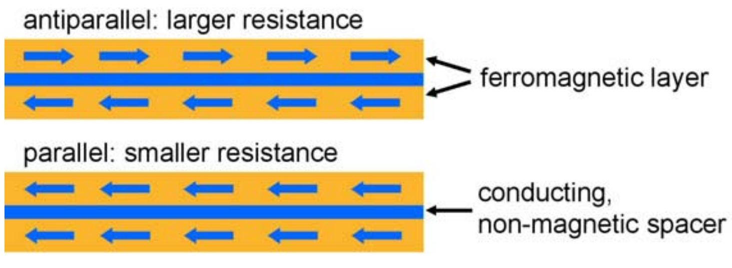

Figure 9: Giant magneto resistance (GMR) effect: The conductivity changes with the relative orientation of thin ferromagnetic layers to each other.

nanometres. The different orientations of the magnetic domains on the surface induce a change in the orientation of the first layer of the GMR element and thus a change in the resistivity which can be measured.
TMR is very similar to GMR and also makes use of adjacent ferromagnetic layers. In contrast to GMR, TMR uses ultrathin non-conducting spacer layers. Thus the

ferromagnetic layers are electrically isolated and electrons can tunnel through this barrier. The TMR effect can also be used to sense the orientation of magnetic domains on the surface of hard disk drives. Another field of application is in so called non-volatile memories (MRAM: magnetoresistive random access memory) which are currently under development. MRAM stores its data in the orientation of magnetic domains using TMR elements. In contrast to today's computer memories, MRAM will remember its data even when the computer is switched off.

Fluorescence of nanoparticles

Colour is a result of different dyes. This is what experience teaches us. But there is another way which is sometimes referred to as physical colour. This can be achieved through well dispersed nanoparticles. The resulting colour is a product of the material used and the size of the particles. Gold nanoparticles for example can be used to provide a reddish color. The advantage of such a physical colour is its extreme stability compared to common dyes which suffer from bleaching. Such nanoparticles have already been used in ancient church windows. Their reddish colour stems from surface plasmons, where electrons are excited collectively. The plasmon resonance frequency of gold nanoparticles is in the green part (~520 nm) of the visible spectrum, thus the visible colour is red. However, certain semi-conducting particles can be used to fluoresce from red to blue under UV only by changing the size of the particles. These semi-conducting nanoparticles are called quantum dots. The mechanism of electron excitement differs from that of metallic particles. Here the bandgap of the semiconductor and the size and shape of the particle (referred to as quantum confinement) determines the colour. Such quantum dots are used in laser diodes.

Figure 10: Nanoparticles (CdSe particles, diameter 3-6 nm) with different diameters fluorescing under UV light. Flad & Flad Communications

c) Complexity

Computation

Perhaps the most popular nanotech consumer products to date are complex electronic logic circuits and memory devices with feature sizes below 100 nm. In order to increase processing speed and memory density, there is a strong economic drive to pack as many circuits into as small of a volume as possible. The results are mobile devices with a myriad of capabilities and commercially available computers that are in many ways able to surpass the cognitive skills and memory of even the most intelligent human beings. As device components shrink, computational speed and memory density continues to become more portable, energy efficient and economical.

3. Products

Textiles and Apparel

A well known disadvantage of fabrics are their tendency to get easily stained. Cloths made of cotton tend to soak up liquids. This drawback can be overcome by increasing the water repellency with fluorinated carbon chains making the cloth more hydrophobic. A well known hydrophobic material is Polytetrafluorethylen (PTFE) or Teflon. This material has been used to produce waterproof clothing such as Gore-Tex, which consists of several laminated layers surrounding a thin Teflon membrane.

Figure 11: A water repellent table set. Flad & Flad Communications, www.nanotruck.de

More recent approaches are based on the use of nanoparticles and dendrimers. Nanoparticles such as SiO_2 increase the washing permanence of the textile finish. Dendrimers have been reported to enhance the water repellency by increasing the fluorine content in the outmost layer of a fabric.

Several textile articles from ties to entire suits have been connected to the “nano” term so far. However the technology is mostly based on the classical fluorinated carbon. The domain of “functional textiles” has grown significantly, and one possible new functionality is the embedding of electronics. Known as “wearable electronics”, these may find applications in sports, medicine and health. Besides the integration of mobile communication technology, keyboards for MP3 players, displays and light effects, more serious functions have been addressed, such as speciality textiles for medical therapy. Silver-containing fabrics have been successfully investigated for treating neurodermatitis. Silver containing socks have been reported for preventing foot odour.

The well known UV protective property of titanium dioxide has also been added to textile fibres. Adding TiO_2 particles to the polymer melt results in a synthetic fibre with embedded UV protection. This product has been successfully used to manufacture cloth with a light protection factor of up to 80. However, the particles shown in Figure 13 have a diameter of 500 nm and thus

Figure 12: A jacket with „wearable electronics“. A MP3 player and keyboard on the sleeve has been embedded. Rosner GmbH + Co.

provide white cotton-like colour due to light scattering.

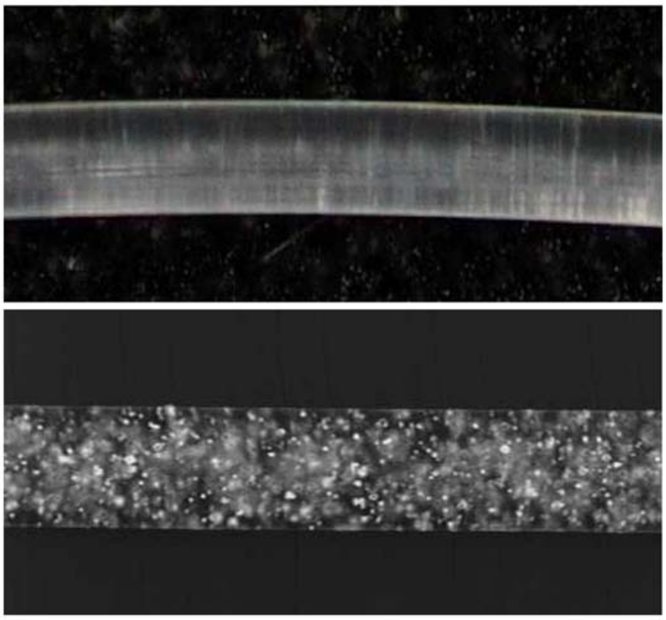

Figure 13: Comparison between an untreated synthetic filament (top) with a treated filament (bottom). The filament is approximately 10µm in width. Titanium dioxide particles allow the

Care Products

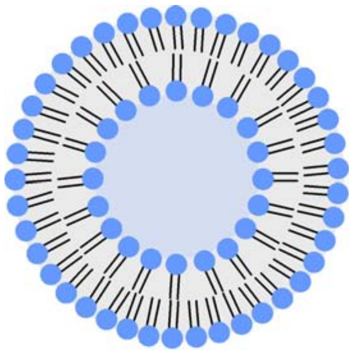

Figure 14: A liposome is a hollow sphere consisting of a phospholipid bilayer.

Today there is a tremendous amount of care products on the market claiming to have some nanotech content. But the idea of putting something very small into a care product is not new. Ultrasmall capsules called liposomes were introduced in a product in 1986 (L'Oreal). Liposomes are vesicles made from a phospholipid bilayer membrane. Their size ranges from below 100 nm to several micrometres. They act as small containers or capsules able to hold and deliver an aqueous content. Their deliveries may vary from therapeutic drugs to vitamins or cosmetic materials in body lotions. Despite having a comparatively simple setup, liposomes are very similar to biological cells.

However, the most common care products featuring nanotechnology are sun care products. Besides the classical approach of using chemical filters to protect the skin by absorbing the dangerous UV light, new physical filters are in use based on well known minerals such as zinc oxide and titanium dioxide. The undesirable whitening effect can be overcome by making these minerals smaller than the wavelength of light. As well dispersed nanoparticles they still offer a stable UV protection for a long time. Both zinc oxide and titanium dioxide containing sun lotions are available from different manufactures.

Figure 15: Left: Skin-care product with photostable UV absorber based on ultra-fine titanium dioxide. Oxonica Healthcare. Right: Sun lotion with zinc oxide as UV absorber. VDI TZ

Another approach based on tiny particles can be found in special toothpastes for sensitive teeth. Teeth consist of a hard protective enamel covering the more sensitive softer dentine. The dentine itself is covered with tiny holes of 2-3 µm in diameter called dentin tubuli (Figure 16 middle). These tubuli form a connection to the underlying pulp and thus to the nerve itself. Normally this extremely sensitive area is well protected under a layer of cementum gum or enamel (see Figure 16 left).

Problems can occur when the gum recedes and the cementum wears down. The exposed tooth neck causes an increase in tooth sensitivity. Toothpastes containing nanoscopic crystals of hydroxyl apatite ($Ca_5(PO_4)_3OH$), which is the main ingredient in natural dentin, act to seal the dentin tubuli, stopping the pain. The toothpaste induces a crystallization of calcium phosphate from saliva using a biocomposite of hydroxyl apatite and protein molecules. The process forms a protective layer of tooth-analogous material (mineralization)[7].

[7] http://www.nanit-active.de/

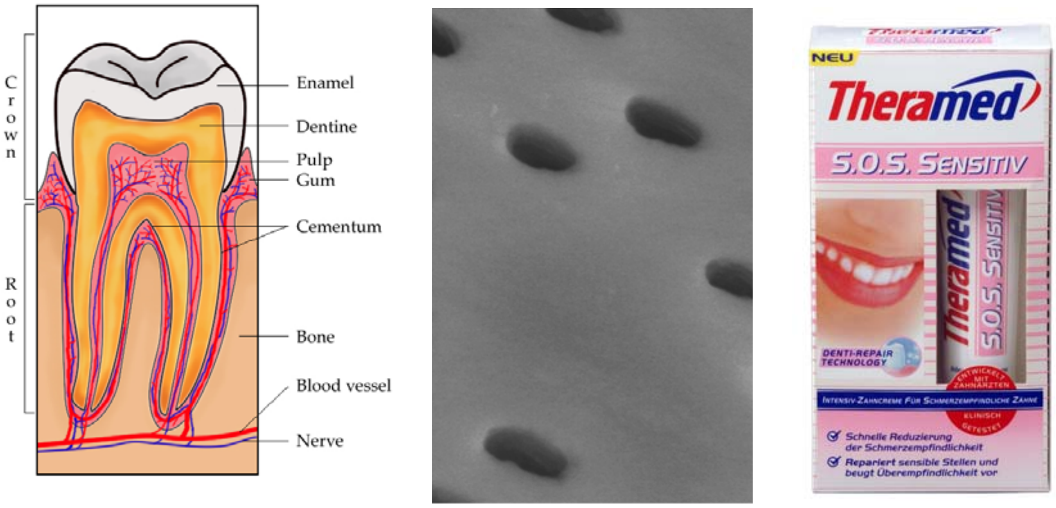

Figure 16: Left: Schematic cross section of a tooth. The dentine is located under a thin layer of cementum. Source: Wikipedia.org. Middle: Scanning electron microscopic image of the microtubule in the dentine. Source: Henkel KGaA. Right: Toothpaste containing hydroxyl apatite against sensitive teeth. Henkel KGaA

Silver can be used in plasters to lower the risk of getting an infection (Figure 17). However the silver does not have to be in form of nanoparticles. Even a plain silver surface works well, although at reduced efficiency.

Figure 17: „Silver Technology" reduces the risk of infections. Beiersdorf AG

A nanotech based approach to home pregnancy tests makes use of the unique optical properties of gold nanoparticles resulting from surface plasmons. The Carter-Wallace home pregnancy test "First Response", uses conventional micrometre-sized latex particles in conjunction with gold nanoparticles (less than 50 nm diameter) to produce a pink colour when exposed to certain hormones produced by pregnant women.

Consumer Electronics

In consumer electronics the buzz word "nano" has become apparent in a well-known MP3 player recently (Figure 18). But does it really mean that nanotechnology has been used to manufacture that product?
Modern MP3 player are without a doubt very small compared to their older brothers, but this fact is not directly correlated to a new technology. However, there are different locations where nanotechnology could have possibly played a role, such as display, memory, battery and surface finish.

Figure 18: A popular mp3 player named „nano", Apple Computer, Inc.

Recent developments have given rise to a giant leap in the size of memory. Today's mp3 players make use of either a mini hard disk or a so-called flash memory, both of which are capable of storing up to several tens of gigabytes. The latter is a large non-volatile storage device similar to an EEPROM (electrically erasable programmable read-only memory) based on the common CMOS manufacturing technique.
Consequently, flash memory is superseding its magnetic predecessor by growing in capacity while reducing the dimensions of its transistors. At present, state-of-art flash production uses 60 nm technology, which refers to the average feature size. This is well below the 100nm limit of the onset of nanotechnology. Flash memory is based on the storage of charges on an electrically isolated transistor gate, called a floating gate. This floating gate can be charged or uncharged, representing the binary states. However, writing and erasing is often done by the quantum mechanical tunneling process (FN Tunneling or Fowler Nordheim Tunneling). In this regard, modern flash memory products truly fall into the realm of nanotechnology. This holds of course for all flash based consumer products without being restricted to the few examples carrying "nano" on their packaging.

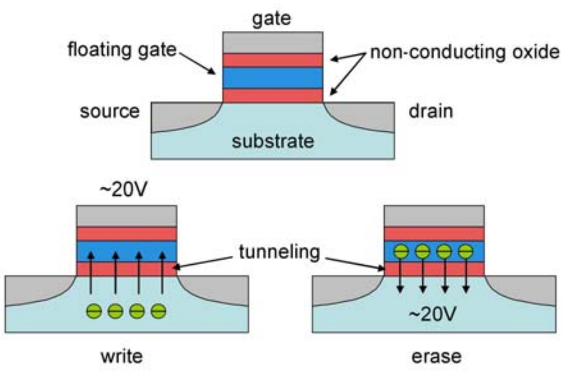

Figure 19: Schematic view of a flash transistor (top) and the write/erase principle (bottom). The floating gate can be charged with electrons by tunneling through a thin oxide layer. VDI Technologiezentrum GmbH

Moreover, the central processing unit, the CPU of every modern computer also makes use of nanotechnology. This is not only because the critical size of the structure of all modern CPUs is well below 100 nm, but also because novel functions have been added.

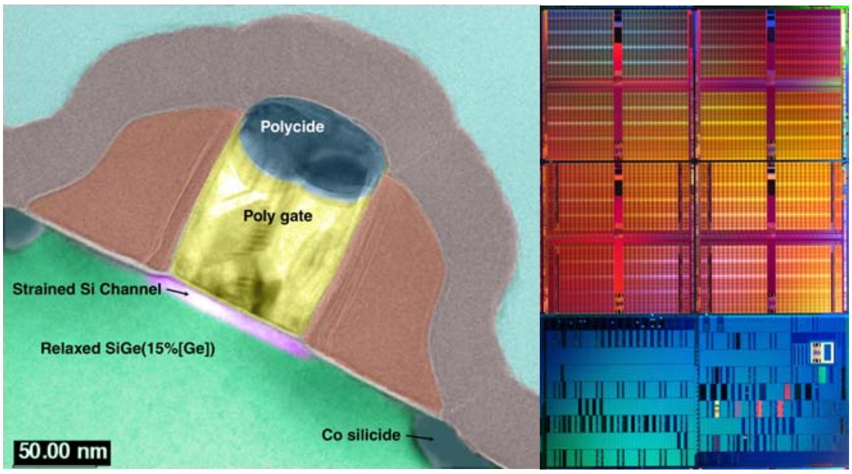

Figure 20: Left: Transistor with conductivity improved silicon channel induced by mechanical stress (strained silicon), IBM. Right: Latest 45 nm technology prototype chip, Intel Corp.

The lattice constant for example of the doped silicon in a field effect transistor can be tuned through mechanical stress. This so-called strained silicon is used to increase electrical conductivity (Figure 20, left).

The read-and-write heads of common hard disk drives make use of the Giant Magneto Resistance (GMR) effect, a quantum mechanical effect which made the enormous storage capacity of today's HDDs possible. The use of GMR technology enabled area densities of well above 100 gigabits per square inch. While the magnetic domains of today's hard disk drive are oriented in-plane, those of the next generation will stand upright (referred to as the perpendicular recording technique, Figure 21 bottom).

More densely packed reading and writing domains requires more sensitive read-and-write heads, which can be achieved through the even more sophisticated Tunneling Magneto Resistance (TMR) effect. In this sense all computer hard disk drives can be

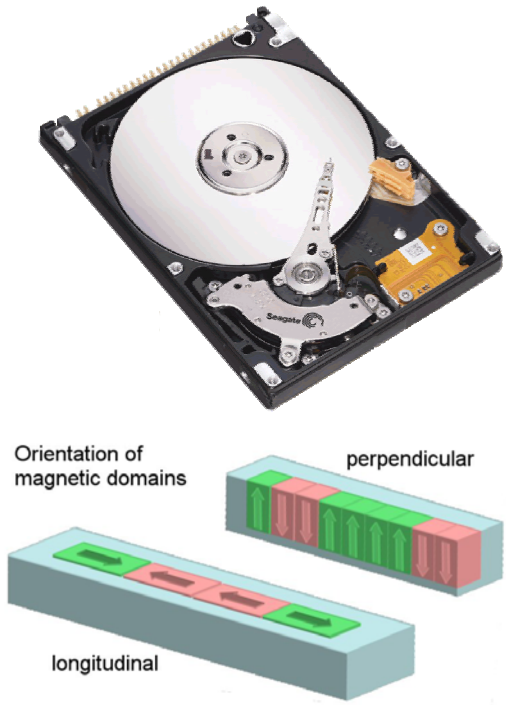

Figure 21: The "Giant Magneto Resistance" Effect (GMR) is widely used in hard disk drives. Seagate Technology LLC (top). The storage density can be increased by changing the orientation of magnetic domains. The perpendicular recording enables higher area densities. VDI Technologiezentrum GmbH (bottom)

regarded as nanotech products.
Another amazing piece of nanotechnology is the light emitting diode (LED) which is widely used today. White LEDs can be found in many illumination applications such as flashlights where they have replaced incandescent bulbs (Figure 22). The benefit is a much longer battery lifetime. White LEDs generate their light in very well defined regions in order to enhance the efficiency (spatial confinement). These regions, called quantum wells, are manufactured with "atomic" precision and with thicknesses of approximately 10 nm. The movement of the charge carriers is restricted to a thin layer resulting in quantized energy levels (quantum confinement). The technology in certain laser diodes is even more advanced: the movement of charge carriers is restricted to small semi-conducting nanocrystals referred to as quantum dots.

Figure 22: Today's flashlights make use of white LEDs providing long battery life times. OSRAM GmbH

Sports

The sports sector in particular has generated many different products related to the word "nano". However, at present it is absolutely unclear to which extent the buzzword "nano" has been supported by serious technology.
Products span from skiing wax ("nanowax") to ultra light bicycles for the Tour de France. At least four different companies worldwide offer tennis rackets reinforced with carbon nanotubes. By making use of a stronger material, the overall weight of the racket can be reduced while the stiffness is maintained or even increased. Such rackets claim to be more responsive than their heavier counterparts (Wilson, Babolat, Völkl, Yonex).
Other sporting goods which make use of carbon nanotubes reinforcement include baseball bats (Easton), badminton rackets

Figure 23: Tennis racquet "Nano-Technology". VDI TZ

(Yonex) and hockey sticks (Montreal Hockey).
Nevertheless, the comparatively high prizes for nanotubes and the lack of detailed technical information, such as a comparison of mechanical properties before reinforcement and after, may leave room for critical questions.
Besides tennis rackets, tennis balls (InMat) and golf balls (NanoDynamics, Nano-S Inc) with nanotechnologically improved properties have been released. The strategy for improving tennis balls is to decrease gas permeability, maintain pressure for longer (twice is claimed; Wilson, Double Core) and therefore to increase life-span (normal tennis balls usually do not last a three set tennis match). However, the golf ball claims to fly “straighter” and to roll better due to a hydrophobic surface are a little more doubtful.

Home improvement

Only a few nanotechnology products can be found in the today’s hardware stores. One example is self-cleaning sheet glass based on titanium dioxide particles (Pilkington Activ™). The self-cleaning layer activates itself after being exposed to UV light, and results inthe breakdown of organic compounds. However, rain is needed to wash away the loosely bonded dirt after decomposition. The same photocatalytic principle has been used to produce self-cleaning clay roof-tiles (ERLUS Lotus®). These clay roof tiles combine the usually contrary properties of hydrophobicity and photocatalysis.

Figure 24: Paint with built-in Lotus effect. Sto AG

Nanoporous materials offer superior thermal insulation. Although silica aerogels are the world champion in lowest thermal conductivity, their brittleness and high price have so far prevented a broader use. Nevertheless, nanoporous materials have been developed in the form of flexible blankets or evacuated panels for better thermal management. (Aspen Aerogels, Va-Q-Tec).
Another example can be found in hydrophobic facade coatings. The famous Lotus-Effect® has been successfully transferred to paint (Lotusan). This paint provides a similar surface microstructure as found on lotus leaves. However, the lotus effect has often been referred to nanotec although the basic structure is rather in the micro range than nano.

Household products

Many different household products have been titled nano or nanotec. Besides cleaning products for glass, tiles and shoes, various different coatings, which are mostly hydrophobic, have been introduced. Even the well known non-stick frying pans have switched to “nano” by using nanocomposites for heavy duty non sticking surface finishes.

Figure 25: Glass cleaner with Nano-Protect®. Henkel KGaA

The idea of using silver for antimicrobial purposes has been used in several products. Amongst filters for air-conditioning the silver has also been introduced in washing machines and refrigerators (Samsung).

Figure 26: Fridge with „Silver Nano Health System™", Samsung

4. Conclusions

The consumer products[8] already available have only begun to exploit the potential of nanotechnology. As has been shown in this report, most consumer products currently available are based on interface effects (with the exception of consumer electronics). However, the major potential that can be expected from the enourmous research investment in nanoscience has not yet reached the consumer. For example, consumer products that exploit quantum effects or the unique electronic properties of carbon nanotubes have only begun to scratch the surface. Furthermore, there are other effects that show promise. For example, molecular recognition is a basic biological principle used in DNA and for other specific bindings such as antigen-antibody on cell surfaces. This effect is widely used in biotech industries such as drug development and diagnostics, but has yet to reach the level of consumer products.

The real promise of nanotechnology might appear when products begin to make use of more than one of these effects. For instance, the incorporation of carbon nanotubes into sports products makes use of their mechanical strength and high surface area to volume ratio, but future products could also exploit their electronic properties and small size, for example connecting different layers in integrated circuits or for building up novel nanotube transistors. Such an approach might lead to revolutionary products that can greatly improve the quality of life of the average consumer.

[8] A comprehensive list of nanotechnological consumer products can be found on www.nanotechproject.org

About Nanoforum

This European Union sponsored (FP5) Thematic Network provides a comprehensive source of information on all areas of nanotechnology to the business, scientific and social communities. The main vehicle for the thematic network is the dedicated website www.nanoforum.org. Nanoforum encompasses partners from different disciplines, brings together existing national and regional networks, shares best practice on dissemination of national, EU-wide and Venture Capital funding to boost SME creation, provides a means for the EU to interface with networks, stimulates nanotechnology in underdeveloped countries, stimulates young scientists, publicises good research and forms a network of knowledge and expertise.

Nanoforum aims to provide a linking framework for all nanotechnology activity within the European Community. It serves as a central location, from which to gain access to and information about research programmes, technological developments, funding opportunities and future activities in nanotechnology within the community.

The Nanoforum consortium consists of:

The Institute of Nanotechnology (UK)	http://www.nano.org.uk
VDI Technologiezentrum (Germany)	http://www.vditz.de/
CEA-Leti (France)	http://www-leti.cea.fr/uk/index-uk.htm
Malsch TechnoValuation (Netherlands)	http://www.malsch.demon.nl/
METU (Turkey)	http://www.physics.metu.edu.tr/
Monte Carlo Group (Bulgaria)	http://cluster.phys.uni-sofia.bg:8080/
Unipress (Poland)	http://www.unipress.waw.pl/
FFG (Austria)	http://www.ffg.at/
NanoNed (Netherlands)	http://www.stw.nl/nanoned/

For further information please contact the coordinator, Mark Morrison: mark@nano.org.uk