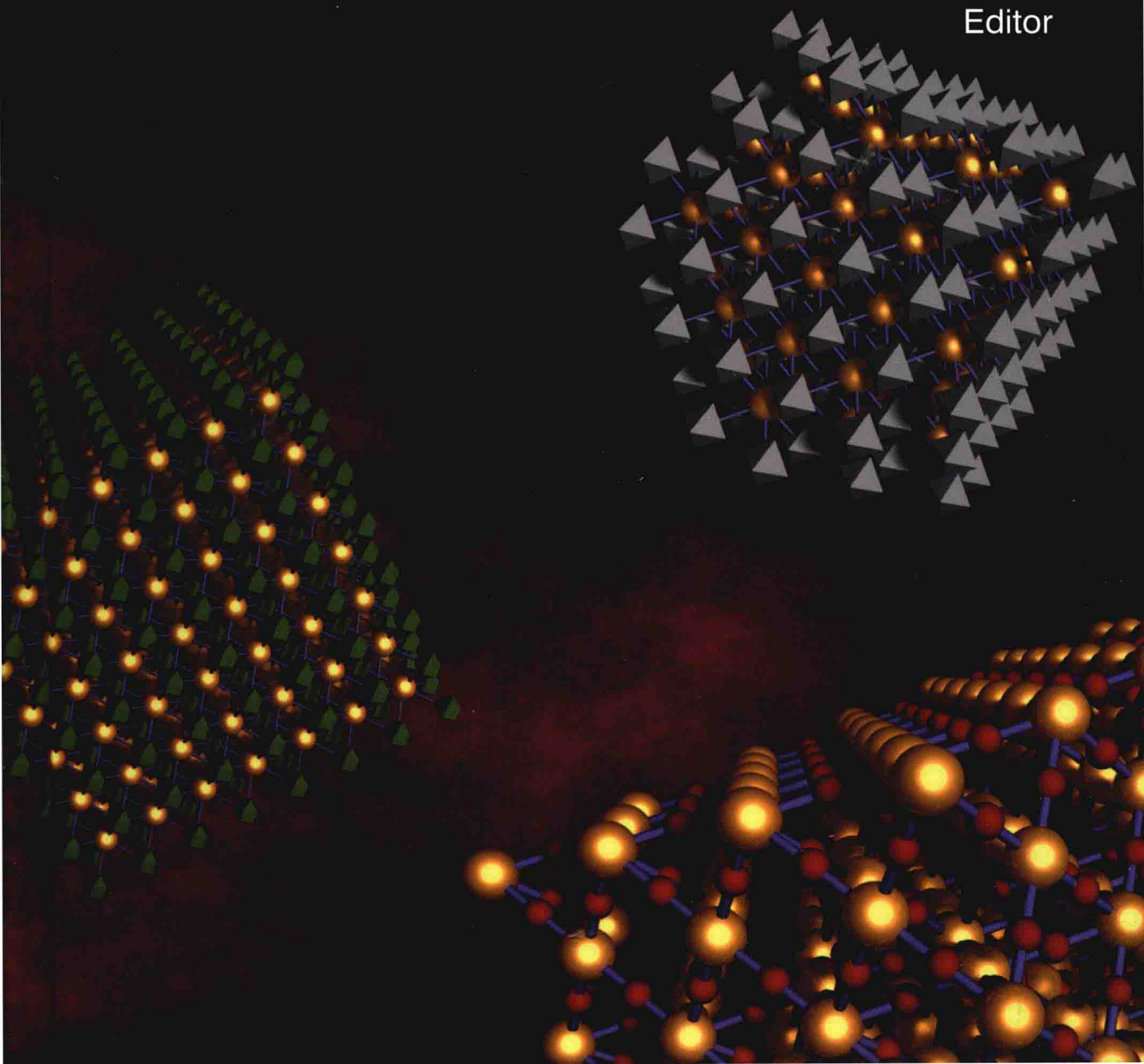


Characterization and Synthesis of Nanostructured Materials

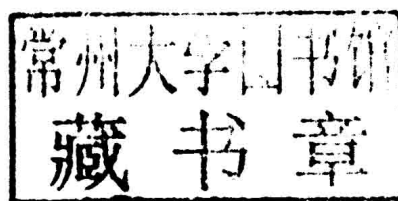
Baron Scott
Editor



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Baron Scott



AURIS REFERENCE LTD.

London, UK

Characterization and Synthesis of Nanostructured Materials

© 2014

Published by

Auris Reference Ltd., UK

www.aurisreference.com

ISBN: 978-1-78154-360-3

Editor: Baron Scott

Printed in UK

10 9 8 7 6 5 4 3 2 1

British Library Cataloguing in Publication Data

A CIP record for this book is available from the British Library

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Characterization and Synthesis of Nanostructured Materials

Preface

Considerable effort has been made to design, fabricate, and manipulate nanostructured materials by innovative approaches. The precise control of nanoscale structures will pave the way not only for elucidating unique size/shape dependent physicochemical properties but also for realizing new applications in science and technology. Nanotechnology offers unprecedented opportunities for improving our daily lives and the environment in which we live.

Nanostructured materials may be defined as those materials whose structural elements - clusters, crystallites or molecules - have dimensions in the 1 to 100 nm range. The explosion in both academic and industrial interest in these materials over the past decade arises from the remarkable variations in fundamental electrical, optical and magnetic properties that occur as one progresses from an 'infinitely extended' solid to a particle of material consisting of a countable number of atoms. Nanostructured materials are one of the highest profile classes of materials in science and engineering today, and will continue to be well into the future. Potential applications are widely varied, including washing machine sensors, drug delivery devices to combat avian flu, and more efficient solar panels. Broad and multidisciplinary, the field includes multilayer films, atomic clusters, nanocrystalline materials, and nanocomposites having remarkable variations in fundamental electrical, optic, and magnetic properties. Environmentally friendly preparation of transparent conducting ITO thin films and One-pot synthesis of gold nanoparticle functionalised mesoporous silica are some examples of nanostructure materials.

It has been already well established that the nanostructured materials is the future materials. Nanostructured materials possess properties superior to those of conventional, coarse grained materials. Hence designing potentially cost efficient and environmentally friendly

products with better performance is a possibility. Among others, nanostructured materials exhibit increased strength, hardness and ductility and provide an opportunity for superplastic forming. When all the procedures in use for the production of nanostructured materials are examined, only severe plastic deformation (SPD) processes exhibit a potential for producing relatively large samples suitable for industrial applications. Recent studies indicate that nanostructuring can be an effective method for increasing the dimensionless thermoelectric figure of merit (ZT) in materials. Most of the enhancement in ZT can be attributed to large reductions in the lattice thermal conductivity due to increased phonon scattering at interfaces. Although significant gains have been reported, much higher ZTs in practical, cost-effective and environmentally benign materials are needed in order for thermoelectrics to become effective for large-scale, wide-spread power and thermal management applications.

The present book focuses on functional aspects of nanostructured materials that have a high relevance to immediate applications, such as catalysis, energy harvesting, energy storage, optical properties and surface functionalization via self-assembly.

—*Editor*

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Chapter 1

Synthesis of Nanoscale Materials

The nanoscopic scale (or nanoscale) usually refers to structures with a length scale applicable to nanotechnology, usually cited as 1-100 nanometres. A nanometre is a billionth of a metre. The nanoscopic scale is (roughly speaking) a lower bound to the mesoscopic scale for most solids. For technical purposes, the nanoscopic scale is the size at which fluctuations in the averaged properties (due to the motion and behaviour of individual particles) begin to have a significant effect (often a few percent) on the behaviour of a system, and must be taken into account in its analysis.

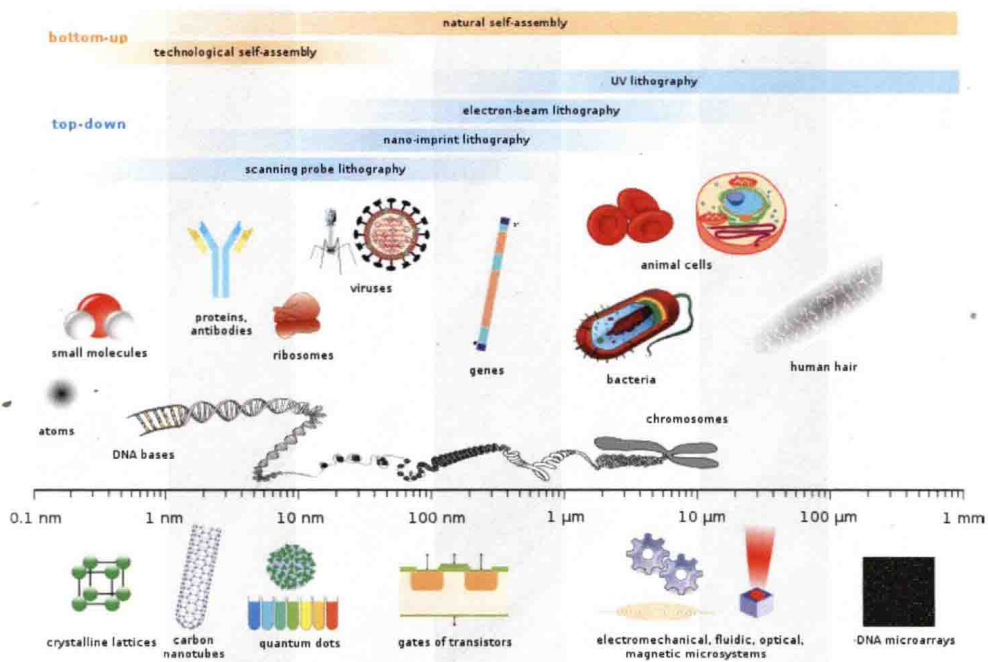


Figure: A comparison of the scales of various biological and technological objects.

The nanoscopic scale is sometimes marked as the point where the properties of a material change; above this point, the properties of a material are caused by 'bulk' or 'volume' effects, namely which atoms are present, how they are bonded, and in what ratios. Below this point, the properties of a material change, and while the type of atoms present and their relative orientations are still important, 'surface area effects' (also referred to as quantum effects) become more apparent – these effects are due to the geometry of the material (how thick it is, how wide it is, etc.), which, at these low dimensions, can have a drastic effect on quantized states, and thus the properties of a material.

Nanostructure

A nanostructure is an object of intermediate size between microscopic and molecular structures. In describing nanostructures it is necessary to differentiate between the number of dimensions on the nanoscale. Nanotextured surfaces have one dimension on the nanoscale, i.e., only the thickness of the surface of an object is between 0.1 and 100 nm. Nanotubes have two dimensions on the nanoscale, i.e., the diameter of the tube is between 0.1 and 100 nm; its length could be much greater. Finally, spherical nanoparticles have three dimensions on the nanoscale, i.e., the particle is between 0.1 and 100 nm in each spatial dimension. The terms nanoparticles and ultrafine particles (UFP) often are used synonymously although UFP can reach into the micrometre range. The term 'nanostructure' is often used when referring to magnetic technology.

GML Nanofilm

Gradient multilayer (GML) nanofilm is an assembly of quantum dot layers with a built-in gradient of nanoparticle size, composition or density. Properties of such nanostructure are finding its applications in design of solar cells and energy storage devices. The GML nanostructure can be embedded in the organic material (polymer), or can include quantum dots made of two or more types of material.

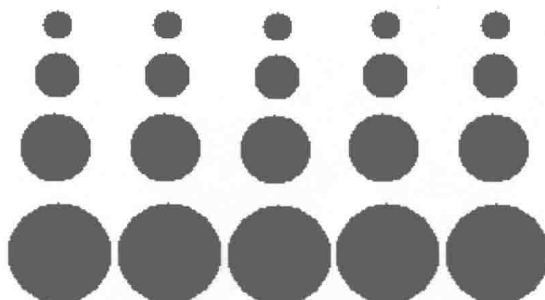


Figure: Schema of GML nanofilm

Photovoltaic Applications

The GML nanofilm only 100 nanometres thick can absorb the entire Sun spectrum (0.3–2.0+ eV). At the same time, gradient of the quantum dots size can create a gradient of the electrochemical potential, acting as an equivalent of built-in electric field inside a nanofilm. This enhances transport of electrons and holes, and improves internal quantum efficiency (IQE) and photocurrent.

Manufacturing

The industrial manufacturing of GML nanofilms represents a challenge. Traditional methods of building nanostructured materials (like spin coating) can't form GML nanostructures, while more effective methods like Atomic Layer Deposition (ALD) or Langmuir-Blodgett "microchemical" method are expensive. The cost-efficient alternative for manufacturing GML nano films is FP ("Flying Particles") method.

Nanocages

Inorganic Nanocages are hollow porous gold nanoparticles ranging in size from 10 to over 150 nm. They are created by reacting silver nanoparticles with chloroauric acid (HAuCl_4) in boiling water. While gold nanoparticles absorb light in the visible spectrum of light (at about 550 nm), gold nanocages absorb light in the near-infrared, where biological tissues absorb the least light. Because they are also biocompatible, gold nanocages are promising as a contrast agent for optical coherence tomography, which uses light scattering in a way analogous to ultrasound to produce in-vivo images of tissue with resolution approaching a few micrometres. A contrast agent is required if this technique will be able to image cancers at an early, more treatable stage. Gold nanocages also absorb light and heat up, killing surrounding cancer cells. The Xia group at Washington University, the original inventors of the nanocages, has functionalized nanocages with cancer-specific antibodies so they specifically attach to cancer cells.

Nanocomposite

A nanocomposite is a multiphase solid material where one of the phases has one, two or three dimensions of less than 100 nanometres (nm), or structures having nano-scale repeat distances between the different phases that make up the material. In the broadest sense this definition can include porous media, colloids, gels and copolymers, but is more usually taken to mean the solid combination of a bulk matrix and nano-dimensional phase(s) differing in properties due to

dissimilarities in structure and chemistry. The mechanical, electrical, thermal, optical, electrochemical, catalytic properties of the nanocomposite will differ markedly from that of the component materials. Size limits for these effects have been proposed, <5 nm for catalytic activity, <20 nm for making a hard magnetic material soft, <50 nm for refractive index changes, and <100 nm for achieving superparamagnetism, mechanical strengthening or restricting matrix dislocation movement.

Nanocomposites are found in nature, for example in the structure of the abalone shell and bone. The use of nanoparticle-rich materials long predates the understanding of the physical and chemical nature of these materials. Jose-Yacaman *et al.* investigated the origin of the depth of colour and the resistance to acids and bio-corrosion of Maya blue paint, attributing it to a nanoparticle mechanism. From the mid-1950s nanoscale organo-clays have been used to control flow of polymer solutions (e.g. as paint viscosifiers) or the constitution of gels (e.g. as a thickening substance in cosmetics, keeping the preparations in homogeneous form). By the 1970s polymer/clay composites were the topic of textbooks, although the term “nanocomposites” was not in common use.

In mechanical terms, nanocomposites differ from conventional composite materials due to the exceptionally high surface to volume ratio of the reinforcing phase and/or its exceptionally high aspect ratio. The reinforcing material can be made up of particles (e.g. minerals), sheets (e.g. exfoliated clay stacks) or fibres (e.g. carbon nanotubes or electrospun fibres). The area of the interface between the matrix and reinforcement phase(s) is typically an order of magnitude greater than for conventional composite materials. The matrix material properties are significantly affected in the vicinity of the reinforcement. Ajayan *et al.* note that with polymer nanocomposites, properties related to local chemistry, degree of thermoset cure, polymer chain mobility, polymer chain conformation, degree of polymer chain ordering or crystallinity can all vary significantly and continuously from the interface with the reinforcement into the bulk of the matrix.

This large amount of reinforcement surface area means that a relatively small amount of nanoscale reinforcement can have an observable effect on the macroscale properties of the composite. For example, adding carbon nanotubes improves the electrical and thermal conductivity. Other kinds of nanoparticulates may result in enhanced optical properties, dielectric properties, heat resistance or mechanical properties such as stiffness, strength and resistance to wear and

damage. In general, the nano reinforcement is dispersed into the matrix during processing. The percentage by weight (called *mass fraction*) of the nanoparticulates introduced can remain very low (on the order of 0.5% to 5%) due to the low filler percolation threshold, especially for the most commonly used non-spherical, high aspect ratio fillers (e.g. nanometre-thin platelets, such as clays, or nanometre-diameter cylinders, such as carbon nanotubes).

Ceramic-Matrix Nanocomposites

In this group of composites the main part of the volume is occupied by a ceramic, i.e. a chemical compound from the group of oxides, nitrides, borides, silicides etc.. In most cases, ceramic-matrix nanocomposites encompass a metal as the second component. Ideally both components, the metallic one and the ceramic one, are finely dispersed in each other in order to elicit the particular nanoscopic properties. Nanocomposite from these combinations were demonstrated in improving their optical, electrical and magnetic properties as well as tribological, corrosion-resistance and other protective properties.

The binary phase diagram of the mixture should be considered in designing ceramic-metal nanocomposites and measures have to be taken to avoid a chemical reaction between both components. The last point mainly is of importance for the metallic component that may easily react with the ceramic and thereby lose its metallic character.

This is not an easily obeyed constraint, because the preparation of the ceramic component generally requires high process temperatures. The most safe measure thus is to carefully choose immiscible metal and ceramic phases. A good example for such a combination is represented by the ceramic-metal composite of TiO_2 and Cu, the mixtures of which were found immiscible over large areas in the Gibbs' triangle of Cu-O-Ti.

The concept of ceramic-matrix nanocomposites was also applied to thin films that are solid layers of a few nm to some tens of μm thickness deposited upon an underlying substrate and that play an important role in the functionalization of technical surfaces. Gas flow sputtering by the hollow cathode technique turned out as a rather effective technique for the preparation of nanocomposite layers.

The process operates as a vacuum-based deposition technique and is associated with high deposition rates up to some $\mu\text{m/s}$ and the growth of nanoparticles in the gas phase. Nanocomposite layers in the ceramics range of composition were prepared from TiO_2 and Cu by

the hollow cathode technique that showed a high mechanical hardness, small coefficients of friction and a high resistance to corrosion.

Metal-Matrix Nanocomposites

Metal matrix nanocomposites can also be defined as reinforced metal matrix composites. This type of composites can be classified as continuous and non-continuous reinforced materials. One of the more important nanocomposites is Carbon nanotube metal matrix composites, which is an emerging new material that is being developed to take advantage of the high tensile strength and electrical conductivity of carbon nanotube materials. Critical to the realisation of CNT-MMC possessing optimal properties in these areas are the development of synthetic techniques that are (a) economically producible, (b) provide for a homogeneous dispersion of nanotubes in the metallic matrix, and (c) lead to strong interfacial adhesion between the metallic matrix and the carbon nanotubes. In addition to carbon nanotube metal matrix composites, boron nitride reinforced metal matrix composites and carbon nitride metal matrix composites are the new research areas on metal matrix nanocomposites.

Another kind of nanocomposite is the energetic nanocomposite, generally as a hybrid sol-gel with a silica base, which, when combined with metal oxides and nano-scale aluminum powder, can form *superthermite* materials.

Polymer-Matrix Nanocomposites

In the simplest case, appropriately adding nanoparticulates to a polymer matrix can enhance its performance, often dramatically, by simply capitalizing on the nature and properties of the nanoscale filler (these materials are better described by the term *nanofilled polymer composites*). This strategy is particularly effective in yielding high performance composites, when good dispersion of the filler is achieved and the properties of the nanoscale filler are substantially different or better than those of the matrix. An example of this would be reinforcing a polymer matrix by much stiffer nanoparticles of ceramics, clays, or carbon nanotubes. It should be noted that the improvement in mechanical properties may not be limited to stiffness or strength. Time-dependent properties could be improved by addition of the nanofillers. Alternatively, the enhanced crystallization behaviour under flow conditions and other physical properties of high performance nanocomposites may be mainly due to the high aspect ratio and/or the high surface area of the fillers, since nanoparticulates have extremely high surface area to volume ratios when good dispersion

is achieved. Nanoparticle dispersibility in the polymer matrix is a key issue, which limits the applicable particle volume fraction and there for also the multi-functionality of the composite material.

Recent research on thin films (thickness <50 micrometre) made of polymer nanocomposites has resulted in a new and scalable synthesis technique, which allows the facile incorporation of greater nanomaterial quantities. Such advances will enable the future development of multi-functional small scale devices (i.e. sensor, actuator, medical equipment), which rely on polymer nanocomposites.

Nanoscale dispersion of filler or controlled nanostructures in the composite can introduce new physical properties and novel behaviours that are absent in the unfilled matrices. This effectively changes the nature of the original matrix (such composite materials can be better described by the term *genuine nanocomposites* or *hybrids*). Some examples of such new properties are fire resistance or flame retardancy, and accelerated biodegradability.

In a recent study, polymeric nanocomposites were fabricated using various one-dimensional carbon nanostructures such as single- and multi-walled carbon nanotubes, as well as two-dimensional carbon and inorganic nanomaterials such as graphene platelets, graphene nanoribbon, single- and multi-walled graphene oxide nanoribbons, graphene oxide nanoplatelets and molybdenum disulfide nanoplatelets as reinforcing agents, to improve the mechanical properties of poly(propylene fumarate) nanocomposites, for bone tissue engineering applications.

Significant mechanical reinforcement (i.e. increases in the Young's modulus, compressive yield strength, flexural modulus and flexural yield strength) were observed at low loading concentrations (0.01-0.2 wt%) of nanomaterials.

The results suggest that mechanical reinforcement is dependent on the nanostructure morphology, defects, dispersion of nanomaterials in the polymer matrix, and the cross-linking density of the polymer. In general, two-dimensional nanostructures can reinforce the polymer better than one-dimensional nanostructures, and inorganic nanomaterials are better reinforcing agents than carbon based nanomaterials.

In addition to mechanical properties, multi-walled carbon nanotubes based polymer nanocomposites have also been used for the enhancement of the electrical conductivity.

Nanofabrics

Nanofabrics are textiles engineered with small particles that give ordinary materials advantageous properties such as super-hydrophobicity (extreme water resistance), odor and moisture elimination, increased elasticity and strength, and bacterial resistance. Depending on the desired property, a nanofabric is either constructed from nanoscopic fibres called nanofibres, or is formed by applying a solution containing nanoparticles to a regular fabric. Nanofabrics research is an interdisciplinary effort involving bioengineering, molecular chemistry, physics, electrical engineering, computer science, and systems engineering. Applications of nanofabrics have the potential to revolutionize textile manufacturing and areas of medicine such as drug delivery and tissue engineering.

Electron microscope image of cotton fibres coated with gold (left) and palladium (right) nanoparticles. The nanoparticles make up just the outline of the fibres in these two images.

A fibre that has a width of less than 1000 nanometres (1000 nm or 1 μm) is generally defined as a nanofibre. A nanoparticle is defined as a small group of atoms or molecules with a radius of less than 100 nanometres (100 nm). Particles on the nanoscale have a very high surface area to volume ratio, whereas this ratio is much lower for objects on the macroscopic scale. A high relative surface area means that a large proportion of a particle's mass exists on its surface, so nanofibres and nanoparticles show a greater level of interaction with other materials. The high surface area to volume ratio observed in very small particles is what makes it possible to create many special properties exhibited by nanofabrics.

The use of nanoparticles and nanofibres to produce specialised nanofabrics became a subject of interest after the sol-gel and electrospinning techniques were fully developed in the 1980s. Since 2000, dramatic increases in global funding have accelerated research efforts in nanotechnology, including nanofabrics research.

Sol-Gel

The sol-gel process is used to create gel-like solutions which can be applied to textiles as a liquid finish to create nanofabrics with novel properties. The process begins with dissolving nanoparticles in a liquid solvent (often an alcohol). Once dissolved, several chemical reactions take place that cause the nanoparticles to grow and establish a network throughout the liquid. The network transforms the solution into a colloid (a suspension of solid particles in a liquid) with a