CHEMISTRY & MATERIALS

FROM MICROSCOPE TO NANOSCOPE

Innovations for Industrial Quality Control

The physical dimensions of nanostructures are far below the diffraction limit of visible light; preventing nanoparticles from being directly imaged by optical microscopy for example. Instead, utilisation of X-ray and electron based methods are widely required. Appropriate techniques are established in R&D, and even visualisations down to the single atom level have been realised[1]. Other nano-analytical characterisation methods are dealing with bulk entities instead of analysing individual structures. However, it is often possible to infer characteristics on the nano-scale out of the bulk properties. This BRIEFING will provide an overview on a number of specific nano-metrology techniques as well as looking at applications in R&D and also those that have already found their way to commercialisation.

The selection of characterisation methods depends primarily on the dimensions of the nanostructures under examination. There are materials that are nano-scale in one dimension such as thin films in electronics, tribological surfaces, or biological membranes. Appropriate analytic tools include microscopic methods such as electron microscopy (EM), scanning probe microscopy (SPM), high resolution optical microscopy each with their various sub-variants, but even different types of spectroscopy; for example based on auger electrons (AES) or photoelectrons (XPS/UPS); or even mass spectrometry (SIMS) are often suitable.

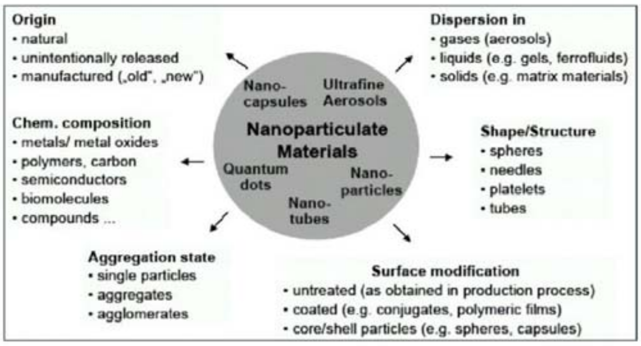

Figure 1: *Parameters for the characterisation of nanoparticulate materials. (Source: Werner et al.[2])*

2D nano-scale materials such as nanofibres and nanotubes are also generally investigated by electron microscopy methods. However, even Raman-Spectroscopy may be used to obtain additional information on 2D-nano-samples[2].

3D nano-scale materials may appear as airborne particles, as components within bulky materials (for example in nanocomposites or nanocrystalline metals), as powders or dispersed in suspensions. Electron microscopy is again often appropriate. However, methods delivering particle size distributions such as dynamic light scattering (DLS), Mobility Particle Sizing (MPS), sedimentation and ultracentrifugation, or zeta-potential analysis may also be suitable and are much more cost effective.

The spectrum of nano analytical techniques is very broad. More detailed information on the individual methods and their technical background may be found in [3]. The decision for a specific method is dependent on the application and the required information (***Figure 1***). In addition aspects of sample preparation, handling and safety are considered. A selection of application examples are presented as follows[4];

Industrial Quality Control

The trend towards utilisation of finely structured materials in industrial applications makes nanoanalytical process and product control increasingly essential:

- *Chemical process control in nanomaterial production*: Numerous nanomaterials, such as CNTs, are now produced on an industrial scale. Production and applications typically require information on parameters such as average length, width, branching, agglomeration, and dispersion. Reliable data generation increasingly relies on existing nanoanalytics such as transmission electron microscopy (TEM).
- *Control of micro- and nano-structured surfaces:* Large scale micro- and nano-structured surfaces play an increasing role in industrial applications (such as self-cleaning surfaces, displays, and lighting layers) and with this the need for efficient process control. Optical Methods such as interferometry are mostly suitable. New approaches in automotive engine construction make use of confocal microscopy to characterise the running surfaces of the interior cylinder walls.
- Nanoanalytic process control is being increasingly utilised in *environmental and medical-technology applications*. Examples include the control of pore sizes of bacteria filters with scanning probe techniques, which is also applied in the production control of medical syringe needles and cannulae.
- *Quality- and defect analysis in semiconductor manufacturing* is increasingly important. Due to the decreasing structure sizes of modern micro chips even smallest structural deviations cause irreversible damage. Combinations of electron microscopic analytics and highly precise

deposition techniques such as electron beam induced deposition (EBID) are utilised to avoid or repair such deviations[5].

Failure Analysis

The analysis of damage caused by material failure is a broad application area for nanoanalytics.

- *Material fracture analysis* is an increasingly common application. It may identify sources of material failure, which is important both for future improvements and the identification of responsibilities. Scanning electron microscopy (SEM) is the most appropriate approach.
- *Analysis of corrosion damage*: Corrosion causes € billion losses every year. Efficient protection is therefore key for many applications; investigation of surface topographies and chemical compositions may give valuable hints. SEM in combination with energy dispersive X-ray spectroscopy (EDX) allows for the identification of local corrosion attacks. The technique is increasingly applied to metallic material monitoring.
- *Nanoanalytics in medical technology* is also gaining importance. An example is the analysis of implants such as intraocular lenses which are used by millions in cataract surgery. However, many lenses suffer from dulling after some years. Failures are often due to nanoscale deviations of the surface structure. Scanning force microscopy (SFM) may be applied to explanted lenses for root cause analysis.

Applied Research

Nanoanalytics is increasingly utilised in areas of material research and is of key importance with respect to the development of new innovations and products.

- *Optimisation of construction materials* based on nano scale additives, such as to mixtures of cement, is very promising. Ultra-high performance concrete (UHPC) based on such additives is giving rise to improved stability with less material consumption[6]. UHPC development has been relying on a strict nano scale control and optimisation of hydration processes during concrete hardening through different techniques of electron microscopy.
- *Pharmacological and bio-medical research* increasingly require nanoanalytics for characterisation. SFM plays an important role in cell biology and is a key to understanding folding processes and functions of proteins.
- *Nanomanipulation*: Controlled manipulation of atoms and nano scale components to set up technically utilisable structures from scratch is a grand vision of nanotechnology. Appropriate research is still at a basic stage. However, the principal possibility based on scanning tunneling microscopy (STM) has been shown.

Impacts

Economic/Industrial

Nanoanalytics plays a key role in development and production of nanotechnology related structures and products. The EC funded "Co-Nanomet programme"[7] identified a number of areas for surface chemical and structural analysis;

- microelectronics
- life sciences, bio-nano-objects
- manufactured nano-objects.

Life sciences and nanomaterials have been indicated as upcoming markets. Microelectronics in contrast has been the main market driver for more than four decades. Decreasing feature sizes continuously require new approaches of failure analysis and quality assurance. The market is very fragmented and an overall market size difficult to determine. Selected market figures for certain areas are provided in ***Table 1***. The market structure for analytical services, instruments and accessories is very complex. Nanoanalytics are used in many technical areas including semiconductors, energy, environment, health, food and agriculture and many more (***Figure 2***).

So far Europe is in a promising position in terms of competitiveness. A key factor is presumably the mostly SME-dominated market.

World market for...	World Market (year)	Source of publication/press release (year of publication)
Failure Analysis Equipment	~$3143 million (2009) ~$4996 million (2015)	Future Markets Inc. (2010)
Microscopy	~$2000 million (2008) ~$3100 million (2014)	BCC (2009)
SEMs	$132.56 million (2010)	Future Markets Inc. (2011)
TEMs	$88.22 million (2010)	Future Markets Inc. (2011)
AFMs	$107.67 million (2010)	Future Markets Inc. (2011)
AFM probes	$62.2 million (2009)	Future Markets Inc. (2010)

Table 1: *World market figures for selected areas in nanoanalytics (the data were taken from press releases or report announcements)*[8,9].

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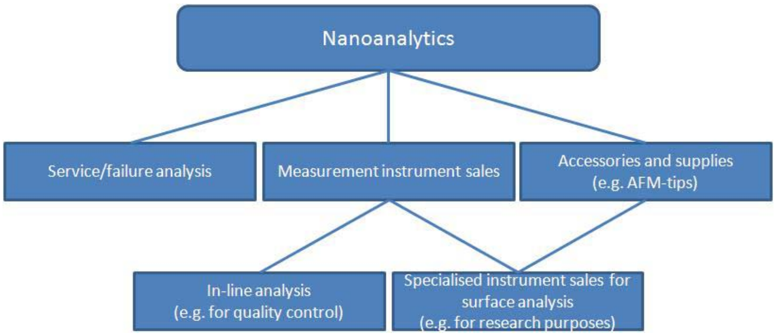

***Figure 2:** Business opportunities in nanoanalytics; generalised market structure (Source: NMTC, unpublished)*

Technology Readiness Levels (TRL)

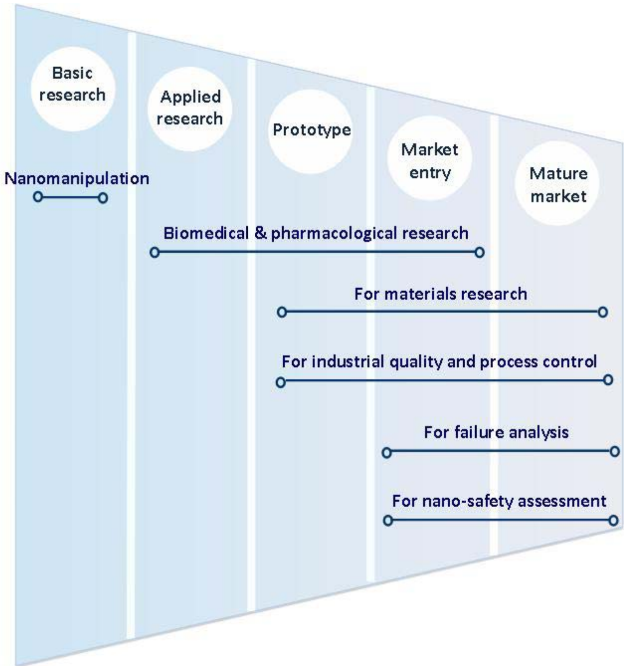

***Figure 3:** TRL for some nanoanalytics applications*

Societal

The ethical and societal dimension of nanoanalytics is related to the availability of analysis tools for risk assessment at largely affordable cost.

Hazard and risk

Exposure to nanoparticles may occur along a variety of pathways, the most common being inhalation, ingestion, and dermal contact. Once exposed, the physical properties of nanoparticles determine their ability to cross biological barriers (translocate) into and within the body. Thus, the route of exposure and physico-chemical properties of nanoparticles will together determine overall exposure. Quantitative characterisation techniques are essential to support the process of exposure and ultimately risk assessment.

Challenges

Nanoanalytics are an inevitable enabling factor for the development of nano-related products. The currently applied methods for the characterization of materials are manifold. However, there are still optimization requirements particularly for applications in material sciences and the bio-medical sector.The combination of nanoanalytics with suitable simulation methods for the prediction of structural and component specific behaviour is only partly solved and even databases for the various methods and systems have to be further improved. Furthermore, the handling of sophisticated instrumentation for non-experts remains an important issue.

EU Competitive Situation

Despite the high quality of European research in nanoanalytics, the US continues to dominate the scene. This is particularly true of research to market transfer for which patents are a useful indicator underlining US-leadership. According to data from the European Patent Office (EPO) US institutions have contributed half of the worldwide

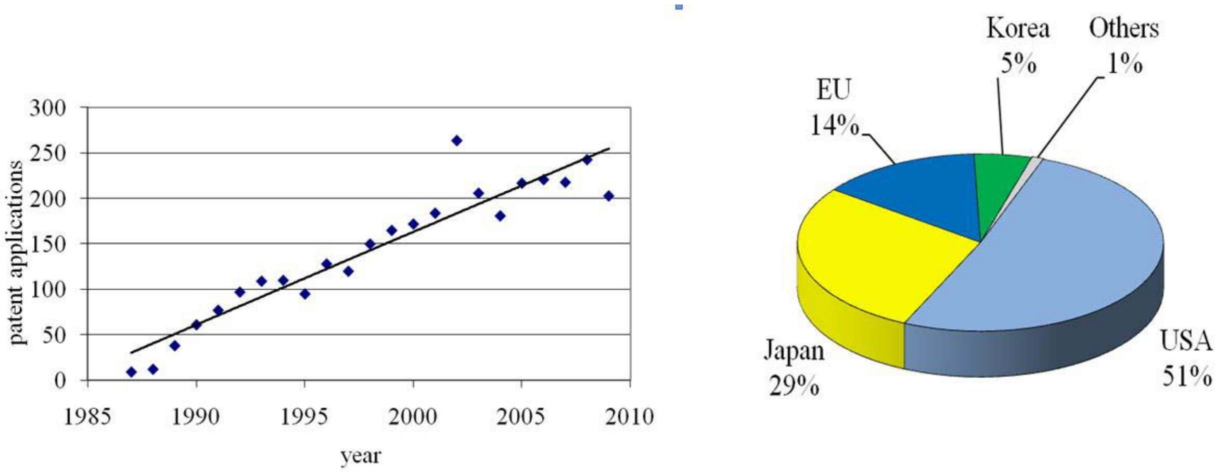

***Figure 4:** Patent applications **Left:** temporal development. **Right:** Country distribution. (Data-source: EPO).*

Company	Remarks	Selected products
Bruker AXS GmbH	Operating company of Bruker Corporation—NASDAQ:BRKR	X-ray microanalysis for SEM and TEM Electron Backscatter Diffraction AFMs Micro X-ray Fluorescence Profilometry
Fries Research & Technology GmbH (FRT)	SME	Metrological surface measuring systems
Jeol Ltd (Japan)	European departments in Europe; Belgium, France, Italy, Germany, Scandinavia, Netherlands, UK	SEMs Analytical instruments for biomedical, pharmaceutical, and environmental fields Electron optics
Nanofocus AG	SME	Profilometry Sensors
Nanotools GmbH	SME	AFM probes
Oxford Instruments	Medium to large scale enterprise	Detectors Coatings thickness measurements Elemental analyser
SPECS Surface Nano Analysis GmbH	SME	Customised systems for surface analysis

Table 2: *European and international major players in nanoanalytics (selection).*

patent applications. With a 14 % share, the EU ranks in the third position[10]. The total number of patent applications has been moderately growing over the past two decades; however, the growth was sub-exponential, which is a downward deviation from the overall trend in nanotechnology.However, Europe is in a comfortable position concerning industrial players in nanoanalytics, who are often backbones of nanotechnology in Europe (***Table 2***).

Summary

- A broad spectrum of nanoanalytical methods exists with much effort spent on increasing the spatial resolution of existing methods.
- Spatially resolving and integral methods represent a trade-off between cost and information depth.
- Most methods are established in R&D and numerous applications have already achieved commercial maturity.
- An increasing industrial uptake of nanoanalytical methods has taken place during recent years. Techniques applicable at a large scale are increasingly essential for new products and innovations.
- Specifically equipped small commercial labs offer various nanoanalytical services and contract research to industry.
- Nanoanalytics plays an increasing role in risk assessment.
- Industries impacted are numerous and include semiconductor, energy, environment, health, food and agriculture and many more. The market is widely fragmented.
- The European competitive position is promising. However, the US and Japan seem to dominate the research-to-application transfer.

Contact Information

Technical: Leif Brand, VDI Technologiezentrum GmbH, brand@vdi.de

Economic: Matthias Werner, NMTC, werner@nmtc.de

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