

Preface

In presenting these chapters with the common theme “Nanocharacterisation”, it is instructive to note the explosive development of nanotechnology over the past few years. Although the term itself is relatively recent, its origins can be traced back to the late 19th century, with the development of colloidal science. The medieval craftsmen who produced the stained glass that adorns many of Europe’s great cathedrals unwittingly used nanotechnology: their addition of gold chloride to molten glass produced tiny, uniformly sized gold spheres (~ 50 nm in diameter) that impart the deep ruby-red colouration that is a characteristic feature of many famous windows; similarly, silver nanocrystals produced an intense yellow colouration.

The use of nanoscale particles with high surface areas has also been exploited for many years in industrial catalysis, and again the preparation of these materials has used “nanotechnology” in various forms.

The anticipation of many of the potential benefits of nanotechnology may be traced back to a lecture “*There’s Plenty of Room at the Bottom*” delivered by Richard Feynman to a meeting of the American Physical Society in 1959. Describing a process by which the ability to manipulate individual atoms and molecules might be developed, Feynman conjectured:

“What could we do with layered structures with just the right layers? What would the properties of materials be if we could really arrange the atoms the way we want them? They would be very interesting to investigate theoretically. I can’t see exactly what would happen, but I can hardly doubt that when we have some control of the arrangement of things on a small scale we will get an enormously greater range of possible properties that substances can have, and of different things that we can do”.

In the course of his lecture, Feynman also noted that scaling issues would arise from changes in the magnitude of various physical phenomena and suggested that electron microscopy would play a key role in the characterisation of these materials.

The term “nanotechnology” was coined and defined in the mid-1970s in a paper presented by Norio Taniguchi (N. Taniguchi, “On the Basic Concept of ‘Nano-Technology’,” *Proc. Intl. Conf. Prod. Eng. Tokyo*, Part II, 1974, Japan Society of Precision Engineering) in which it was suggested that it “*consists of*

the processing of, separation, consolidation, and deformation of materials by one atom or one molecule.”

Subsequently, this basic definition was explored in greater depth by Eric Drexler, who vigorously promoted the technological significance of nanoscale phenomena and devices. [*Engines of Creation: The Coming Era of Nanotechnology and Nanosystems: Molecular Machinery, Manufacturing, and Computation*”, (ISBN 0-471-57518-6).]

At the time of writing “nanotechnology” embraces a large (and growing number) of techniques that are used to create and characterise structures on a size scale below ~ 100 nm. Included in these are methods used for the fabrication of nanowires, lithographic techniques routinely used in semiconductor fabrication, focused ion beam (FIB) machining and related techniques used for the production of micro-electro-mechanical systems (MEMS) and molecular self-assembly.

In the early 1980s two significant developments had a major impact on characterisation aspects of nanotechnology: the invention of the scanning tunneling microscope and the synthesis of small carbon clusters. The development of this instrument in 1981, for which Gerd Binnig and Heinrich Rohrer were awarded the Nobel Prize in 1986, followed on exactly 50 years after the development of the first transmission electron microscope in 1931 by Max Knoll and Ernst Ruska, the latter sharing (somewhat belatedly) the same Nobel Prize. This has in turn spawned a plethora of other scanned probe microscopy techniques including atomic force microscopy, magnetic force microscopy, electrostatic force microscopy and others.

The discovery in 1985 of single, closed-shell carbon nanostructures (e.g. C_{60}) known collectively as fullerenes, by Harold Kroto and his colleagues, for which they also were awarded the Nobel Prize in 1996, and the recognition of carbon nanotubes, provided much of the impetus for what would become an unprecedented and explosive worldwide development and interest in nanostructures.

These developments have driven a need for ever-more powerful techniques for structural and chemical characterisation on the “nanoscale” and “nano-characterisation” – the theme of this book, now encompasses a diverse range of techniques that are the essential tools underpinning much of nanotechnology.

In attempting to give an overview of the different techniques now in regular use in nanocharacterisation we have been necessarily selective and we note that other microscopies are still developing that will certainly find a place in the armoury with which nanotechnologists will pursue their quest for ever-smaller and tighter-controlled structures.

In the chapter devoted to high-resolution (transmission) electron microscopy David Smith illustrates how this technique has evolved into a widely used tool in modern nanostructure research, highlighting the problems relating to interpretation of image contrast, as well as providing numerous examples showing how HRTEM has been used to provide unique insights into local microstructure of nanocrystalline materials.

The development of the scanning transmission electron microscope in the 1970s by Albert Crewe and colleagues produced instruments that could use the

signals generated by scanning an electron beam across a thin specimen in a controlled manner. The chapter by Andrew Lupini, Stephen Pennycook and their coworkers outlines this technique and demonstrates how the recent application of aberration-correcting devices in STEM instrumentation is now capable of producing sub-Angstrom imaging and spectroscopy of nanostructures.

Complementing the above are the various scanned probe microscopy techniques that have emerged following the initial development of the scanning tunneling microscope. These instruments rely on a variety of surface/probe interactions and delicate rastering mechanisms to obtain images with extreme depth sensitivity to various parameters thus revealing many physical and electronic properties with atomic resolution. The additional ability to interact with *individual* atoms on surfaces in a precisely controlled manner also opens up an exciting range of opportunities for nanoscale manipulation and fabrication. Martin Castell in his chapter provides an overview of this field, and explores in detail the use of these techniques in nanoscience.

In addition to structural information, local chemical composition, bonding and electronic states are key aspects of nanostructures. A range of spectroscopic techniques is now available for probing local structures on the atomic scale. Among these, electron energy-loss spectroscopy and energy dispersive X-ray analysis have emerged as the most powerful and widely used. These techniques probe, respectively, the energy loss of electrons passing through a thin specimen and the X-rays generated by the incident electron beam. The chapter by Rik Brydson provides an overview of the physical principles involved in these and demonstrates how they are now being used to probe local chemistry and bonding at the atomic level.

In many applications of nanotechnology the measurement of the magnetic and electrical properties of individual nanoscale objects is becoming increasingly important. Relatively recent instrumental developments have enabled the technique of electron holography, first proposed by Gabor in 1947, to be used, to obtain measurement of these. Rafal Dunin-Borkowski and coworkers describe the theory and practice of this technique and its application to a range of important nanostructured magnetic and electronic materials.

As nanostructures become smaller, their 3-dimensional shape assumes much greater importance. This is particularly the case for supported catalysts, where active sites may be determined by such entities. Although electron tomography had been previously applied successfully to biological structures it has only recently been extended to for applications in nanoscience. Paul Midgley and Mathew Weyland survey the instrumental, theoretical and computational requirements of this important technique and illustrate how it can be used to gain 3-dimensional information from a wide range of technologically important materials.

The ability to carry out or induce chemical reactions on a very small scale is also crucial to many aspects of nanotechnology and the ability to observe these *in situ* is a particularly powerful combination. This can be achieved with specially modified instrumentation that allows a controlled, gaseous environment around the specimen. In the concluding chapter, Pratibha Gai gives an

account of the design and use of an environmental transmission electron microscopy facility including a description of the physical principles involved in its design together with numerous case histories describing some of the insights gained into some important chemical processes.

In summary, our aim in preparing this book has been to gather together a selection of articles written by internationally recognised experts that describe some of the characterisation techniques that are currently used in studies of nanostructured materials.

We hope that the handbook will provide a valuable resource to all involved in the characterisation of nanomaterials.