

Cheminanotechnology: Nanotechnology for Chemistry and Chemical Engineering

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A well known scientist was recently heard to comment that the word *nano* is Greek for funding. How much truth is there in this jest – is nanotechnology just marketing hype to make the work of some scientists sound trendy and new or is there some merit to the term? Is it just a new name to an old concept or is it, as many claim, a revolutionary way of thinking that will change the face of science and technology? There are claims that billions of dollars are spent worldwide on nanotechnology research. But where has all this research suddenly appeared from? What were these people doing before the term nanotechnology came into widespread use and became favoured by the funding agencies? A cynic might rightly be amused at how so many people have managed to reinvent themselves.

At this point I will have to confess that I fall into the category of someone who may have benefited from using the term nanotechnology in funding applications and also someone who is reinventing themselves as a nanotechnologist even to the extent of offering the first nanotechnology degree in New Zealand. But is this a blatant piece of marketing or is there some substance to this claim? *If I am part of the nanotechnology fraternity how can I be trusted to give an unbiased answer anyway? The reader will have to make this judgement.*

Here I give my opinion on these issues. For those who choose to buy into this approach, I would also like to define a new term, *cheminanotechnology*, to represent the most pervasive nanotechnology which is that which applies to chemical processes.

Most commentaries on nanotechnology start with reference to Eric Drexler,¹ who is credited with coining the term, and then proceed to discuss physicist Richard Feynman's assertion that *there is plenty of room at the bottom*,² by which he meant the advances that remain to be made in manipulating and controlling things on the small scale. After this point, views diverge. Nanotechnology can mean little machines that will pump miniscule volumes of liquid, or it can refer to some new development in fabrics that repel water. Many people understand nanotechnology to refer only to miniature electromechanical devices. Some try to separate nanotechnology from nanoscience. Most would agree that nanotechnology deals with the very small scale - things measured in nanometres.

So how does nanotechnology apply to chemistry and chemical engineering? Chemistry can be loosely described as the study of the formation, properties, and interactions of molecules, while chemical engineering is the control of chemical processes on a large scale. It

has been known since at least the time of Lord Kelvin³ and J. Willard Gibbs⁴ that the thermodynamic properties of a chemical substance are not constant but are in fact affected by the size of the piece of the substance being studied. It appears that some people have not been taught this in their undergraduate courses or they have forgotten these details. For example, everyone *knows* that at 1 atm pressure water boils at 100 °C. However, this is true only of relatively large volumes of water. A droplet of water of 5 nm radius will boil at 95.9 °C.⁵ The physics behind this has been understood for over a hundred years. Similarly, melting points are affected by size; gold, which normally melts at 1064 °C, will melt at temperatures as low as 350 °C when it is a 2 nm particle.⁶

At the nanoscale, not only do these physical properties change but enthalpies of fusion, vaporisation, and chemical reaction change. These can affect the equilibrium of a chemical reaction or can lead to chemical reactions being possible that do not take place on larger particles. An early example is the observed change in the nickel-nickel carbonyl equilibrium.⁷ A more recent example is the discovery that small particles of gold exhibit catalytic behaviour.^{8,9} Previous studies on larger particles of gold showed no catalytic activity, and the change is known to be chemical rather than depend upon the increase in surface area per mass as a substance is divided up into smaller pieces. Properties thought to be characteristics of the substance start to become inconstant at small sizes, and at the nanometre level the effects have dramatic results.

It is not only chemical reactions but also fluid flows that change at small size. When dealing with liquids at small scales, that indispensable engineering concept, the Reynolds number (the dimensionless ratio of viscosity to momentum) is usually less than unity, and handling fluids becomes quite a different task with the intuitive notions of the flow and behaviour of a liquid being overturned.^{10,11}

Most of these changes to the properties of substances at small scales have been known to chemists and chemical engineers for many years. What, then, has changed that enables us to claim the term nanotechnology for our work? There are two key areas where there have been changes that justify the application of the term nanotechnology to chemical research.

We now have techniques that can look at, or work with, single molecules to establish the properties of molecules individually rather than as an average of a collection. A good example here is the scanning probe microscope (SPM) that enables us to visualise single atoms and even

electron waves¹² in a way we may never have thought possible. Now we can see defects in surfaces at which catalysis may be occurring,¹³ whereas previously we knew that they must exist but could only infer their properties by other means. We can stretch single molecules and obtain directly physical properties^{14,15} and thermodynamic data from force measurements on the single molecule rather than the large numbers of molecules in a calorimeter or a spectrophotometer.¹⁴ We can look at the effect of possible new drugs on a single live bacterium rather than on a whole population of bacteria.¹⁶

Not only do we have new techniques but we have new materials that were not available previously. Challenges still lie in determining how these new products can be used, but they are providing opportunities for new and innovative exploration into fields ranging from medicine to mineral processing. Examples include carbon nanotubes¹⁷ (people were wondering what could be done with these but applications are now appearing) and titanium dioxide nanotubes.¹⁸ We can now use our understanding of the adhesion forces we observe in nature, such as a gecko clinging to a wall solely by means of van der Waals forces,¹⁹ and mimic these structures in synthetic adhesive materials.²⁰ A further spectroscopic technique of interest to chemists is surface-enhanced Raman spectroscopy whereby the signals can be enhanced up to 10^{15} times for molecules adsorbed onto clusters of small particles of gold or silver.²¹

The blurring of the traditional disciplinary boundaries between chemistry, physics, and chemical engineering is reflected in the lack of clear distinctions between the branches that make up nanotechnology. Nevertheless, cheminotechnology can be delineated as a subset of nanotechnology that is focused on understanding the effect that very small size has on chemical reactions, and the subsequent use of this understanding in new product and process development.

So, while at times I am a nano-cynic, I think the emphasis on nanotechnology is a useful guide to one's thinking and has at least some basis in actual practice. Although much of the science relating to nanotechnology may not be entirely new it reflects a major change in the tools and techniques available for studying materials and processes at the nano scale. New materials and methods have been developed utilising the peculiar properties of the nanoscopic realm and many applications remain to be discovered or developed.

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