

## World's thinnest nanowires

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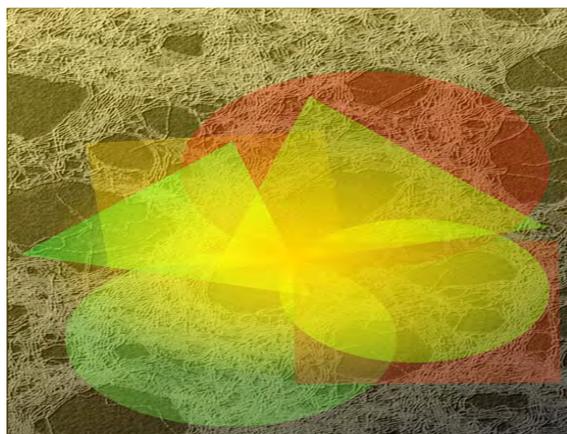


Figure 1.

Dawn of a beginning of something new and exciting - materials chemistry and nanochemistry emerging fields that never tire of re-inventing themselves.

Nanowires are amongst the most actively studied nanostructures in the field of nanoscience as witnessed by the impressive number of citations this field has accrued in a short period of time since their discovery. Its blossoming was enabled by nanochemistry breakthroughs that facilitated the reproducible, scalable and cost-effective synthesis of such structures. One drawback of all these syntheses was the 10 nm lower limit in the diameter of the nanowires that could be produced. While exploring the synthesis-structure space in the pnictide chalcogenide system we serendipitously discovered the world's thinnest nanowires with unprecedented narrowness of 1.6 nm that corresponds to just a few unit cell widths. Protected by a sheath of capping-ligands these ultrathin nanowires can be made soluble in polar and non-polar solvents.

An exciting prospect that has surfaced from studies of this novel class of ultrathin nanowires is the emergence of their polymer-like properties, a discovery that allows one to probe the fuzzy interface between nanowires and molecular entities.

Questions that immediately arise are whether we can observe polymer-like topological properties in inorganic nanowires, can we crosslink and electrospin them to form gels, fibres and meshes, can they display high electrical conductivity yet low thermal conductance pivotal to enhancing the efficiency of thermoelectric devices, can we couple molecular properties like monodispersity with quantum size effects of nanoscale materials, and what would the interface between these two worlds look like?

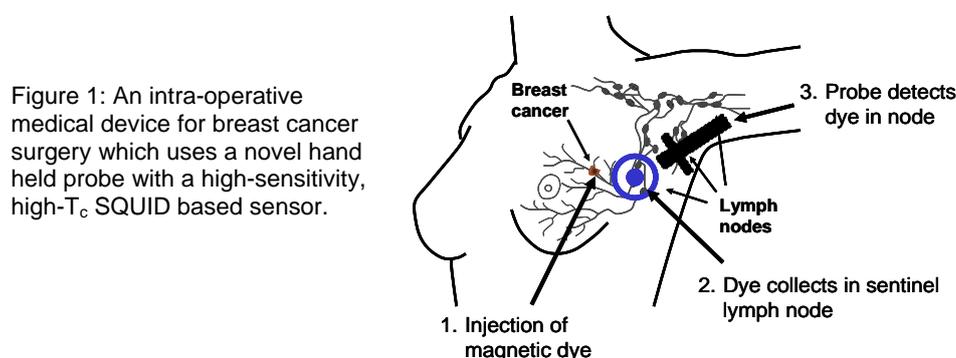
Such results could open new avenues of exploration in the ill-defined size regime where molecular meet nanoscale properties. One can envision a new platform of polymer-like nanowires where the chemical and physical properties of inorganic materials are fully embodied in an architecture which shows the topological and self-assembly properties of polymers.

## Healthcare Biomagnetics: in vivo sensing, moving and heating of magnetic nanoparticles for diagnosis and therapy

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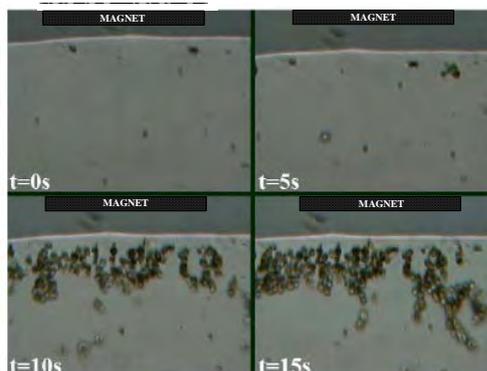
The emerging field of 'endomagnetics' – the sensing, moving and heating of magnetic nanoparticles in the human body for diagnostic and therapeutic purposes - will be reviewed. Examples will be given for each of the modalities, including the following:

**Sensing:** A high- $T_c$  SQUID based sensor system, with a room temperature hand-held probe, designed for use in a hospital operating theatre to detect breast cancer sentinel lymph nodes (Figure 1). The system is currently being evaluated in patients, and has been used successfully in seven operations.



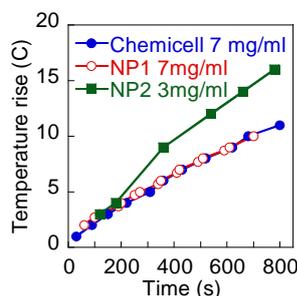
**Moving:** A high field-gradient magnetic actuator designed to capture magnetic nanoparticle loaded haematopoietic stem cells for the treatment of atherosclerosis. Bench-top (Figure 2) and animal trials are under way to establish the efficacy of such a therapy, with promising results.

Figure 2: Microscope images showing the attraction of magnetically labelled CD133 stem cells towards a magnet placed at the top of a cells-in-water droplet. Scale: each cell is ca. 10  $\mu$ m in diameter.



**Heating:** Magnetic field hyperthermia treatment for superficial and, as a long term goal, metastatic cancer, using antibody-targeted magnetic nanoparticles. Work is progressing on several fronts: the synthesis of improved magnetic particles for heat transduction (Figure 3), the engineering of new high-frequency drive circuits to produce rf fields in controlled geometries, and cell and animal studies of antibody-nanoparticle conjugation and tumour targeting.

Figure 3: Magnetic field heating characteristics of a commercial nanoparticle suspension and two lab-synthesised samples – all are magnetite/maghemite based. Measurements recording in an rf field of magnitude 140 Oe and frequency 138 kHz.



**From foams to dry water:  
Phase inversion of nanoparticle-stabilised materials**

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Phase inversion of particle-stabilised emulsions from oil-in-water to water-in-oil can be achieved either by increasing the particle hydrophobicity at constant oil:water ratio (transitional) or by increasing the oil:water ratio at fixed particle wettability (catastrophic).<sup>1</sup> Here, we describe for the first time the corresponding inversion of particle-stabilised air-water surfaces, not achievable up to now with surfactant molecules. The nanoparticles are those of fumed silica, made hydrophobic by reaction with dichlorodimethylsilane. Inversion from air-in-water foams to water-in-air free flowing powders is effected *via* both transitional and catastrophic inversion.

The novel materials so produced represent a way of encapsulating air or water, with the adsorbed particle layer providing a means to control the release of gaseous or liquid components respectively.



Reference:

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**Soft processing for ceramics:  
Single-step fabrication of nano-structured oxide ceramics  
(particles, films, integrated layers and patterns) from solution without firing**

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Since 1989 when we found a method to fabricate BaTiO<sub>3</sub> film on Ti substrate in a Ba(OH)<sub>2</sub> solution by Hydrothermal Electrochemical[HEC] method at low temperatures of 60-200 °C, we have proposed an innovative concept and technology, “Soft Processing” or “Soft Solution Processing,” which aims low energetic (=environmentally benign) fabrication of shaped, sized, located, and oriented ceramic materials in/from solutions. It can be regarded as one of bio-inspired processing, green processing, or eco-processing.<sup>1,2)</sup> When we have activated/stimulated interfacial reactions locally and/or moved the reaction point dynamically, we can get patterned ceramic films directly in solution without any firing, masking or etching. Those Direct Patterning methods differ from previous patterning methods which consist of multi-step processes, for example: (1) synthesis of particles of compounds or precursors, [When this synthesis is done in a solution it is called “Soft Chemistry”.] (2) Dispersion of the particles into a liquid (“ink”), (3) patterning of the particles on a substrate by printing of the “ink”, (4) consolidation and/or fixing of the particles’ pattern by heating and/or firing at high temperatures. (5) Those processes would cause cracking and/or peeling of patterned films due to the shrinkage of printed powders by sintering during heating and/or firing.

The notable feature of Direct Patterning is that each reactant reacts directly on site, at the interface with the substrate. Therefore, the chemical driving force of the reaction,  $A+B=AB$ , can be utilized not only for synthesis but also for crystallization and/or consolidation of the compound AB. It is rather contrasting to general patterning methods where thermal driving force of firing is mostly used for the consolidation of the particles. 3) We have developed the Direct Patterning of CdS, PbS, and CaWO<sub>4</sub> on papers by ink-jet reaction method and LiCoO<sub>2</sub> by electrochemically activated interfacial reactions.<sup>4)</sup> Furthermore, we have succeeded to fabricate BaTiO<sub>3</sub> patterns on Ti by a laser beam scanning and carbon patterns on Si by a needle electrode scanning directly in solutions.<sup>5)</sup> Recent success in TiO<sub>2</sub> and CeO<sub>2</sub> patterns by Ink-jet deposition, where nano-particles are nucleated and grown successively on the surface of substrate thus become dense even below 300 °C, will be presented.<sup>6)</sup> Transparent films of several hundred nm thick can be obtained by 20 times of ink-jet scanning during 15-30 min. [Fig. 1]

As a development of Hydrothermal Electrochemical[HEC] method, we have proposed a new strategy: “Growing Integration Layer[GIL] method”, which can provide well-adhered integrated/graded layers: Titanate/TiO<sub>x</sub>/Ti or Titanate/TiO<sub>x</sub>/Ti-alloys and/or metallic glass(es) at RT-150 °C in a solution. This [GIL] strategy can be applied for many areas of functional ceramics.<sup>7-9)</sup>

In addition, our recent results on mono-dispersed nano-particles of CeO<sub>2</sub>(10), (Hf,Eu)O<sub>2-x</sub>(11), Fe<sub>3</sub>O<sub>4</sub>(12), etc. [Fig. 2] will be presented.

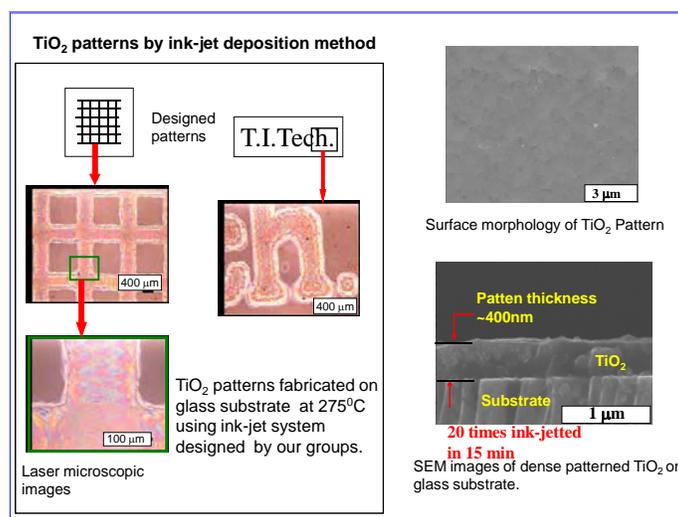
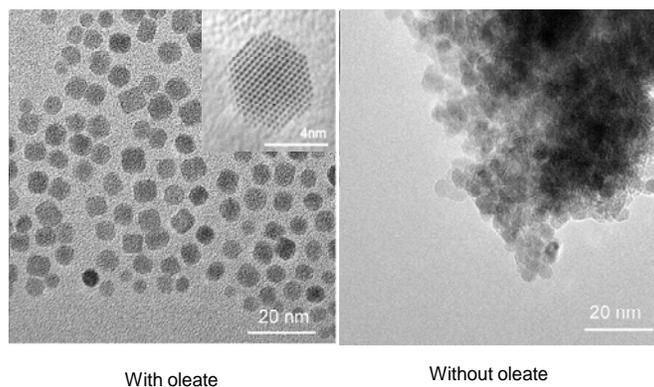


Figure 1.

TEM observation of CeO<sub>2</sub> 200°C, 6hours with oleate



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Figure 2.

Reference:

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## Parliament's understanding of science

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In most western countries our Parliament are desperately short of people with any scientific background. The challenge to us all is how to change that by encouraging the science community to reach out to Parliaments and vice versa. Andrew Miller's contribution will describe the role he has played in attempts to remedy the situation. He will describe the work of the Parliamentary & Science Committee <http://www.vmine.net/scienceinparliament/sip.asp> and its sister organisation The Parliamentary IT Committee <http://www.pitcom.org.uk/>.

He will describe the Royal Society pairing scheme within which he spent some time helping Dr Nguyen TK Thanh to understand the role of an MP and also spent time with her improving his understanding of her research programme. She is one of six North West scientists who have been partnered with Mr Miller covering fields as diverse as animal husbandry to black holes! Mr Miller will argue for an expansion of this approach as he believes that we will see a more and more irrational response towards scientific endeavour on the part of parliamentarians if there is not a system of continuous education targeted at our legislators.

## Printable photovoltaics using colloidal quantum dots

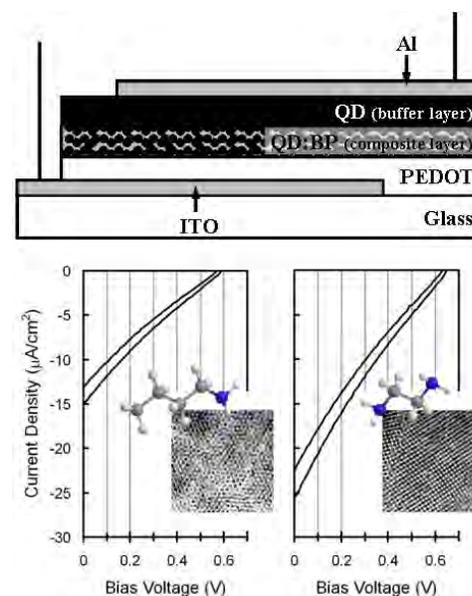
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Organic photovoltaic cells (OPVCs) are expected to be next-generation solar energy conversion devices because they have the potential to be flexible and low cost. Many device structures have been proposed, such as Schottky junction, flat (bilayer) heterojunction (FHJ), and bulk heterojunction (BHJ) structures. Above all, the BHJ devices are thought to be promising for increasing the energy conversion efficiency ( $\eta$ ) of OPVCs. So far, BHJ devices have been fabricated by blending fullerene derivatives or CdSe colloidal quantum dots (QDs) into conjugated polymers, or by utilizing the phase separation of donor and acceptor conjugated polymers. However,  $\eta$  and durability remain insufficient for practical use.

Conjugated polymers can be dissolved in various solvents and, thus, are useful in fabricating BHJ devices via solution processes. However, the conjugated polymers have low carrier drift mobility ( $\mu$ ) and they are usually easily degraded. On the other hand, low-molecular-weight organic semiconductors (low- $M_w$  OSs), e.g., pentacene, rubrene, and porphyrin, generally have higher  $\mu$  ( $>10^{-2}$   $\text{cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ ) and higher durability compared with polymeric semiconductors because of their high crystallinity. However, these low- $M_w$  OSs are usually insoluble and not suited for solution processes with a few exceptions. One example is tetrabenzoporphyrin (BP), which is derived from a precursor with four bicyclo structures (CP) by elimination of four ethylene molecules. Fullerene derivatives, such as [6,6]-phenyl  $\text{C}_{60}$ -butyric acid methyl ester, and wide-gap semiconductor (e.g., CdSe and InP) QDs have very little absorption at infrared (IR) wavelengths. Type IV-VI semiconductors, such as PbS, PbSe and PbTe, are known as narrow-gap semiconductors and, thus, IV-VI QDs are expected to be good candidates as acceptor materials in BHJ solar cells to improve the coverage of the solar spectrum. In addition, the PbSe QD solar cell (QDSC) is thought to attain maximum  $\eta$  up to 60% due to carrier multiplication. Based on these expectations, several groups have proposed QDSCs consisting of PbSe QDs and conjugated polymers.

Recently, we reported a solution-processed polymer-free photovoltaic device consisting of PbSe colloidal QDs and BPs that has higher  $\mu$  and higher durability compared with polymeric semiconductors [1]. In that study, FHJ and BHJ structures were fabricated and the current-voltage characteristics of the devices under near-IR illumination were studied. Consequently,  $\eta$  of the BHJ device was found to be much higher than that of the FHJ device. However, the photovoltaic performance of the BHJ device (ITO/PEDOT/BP:QD/Al) was still low. The low  $\eta$  was thought to be due to the poor electrical contact between the QDs and BP (or between QDs) because of long-chain ligands (oleic acid) which are present on the surface of the QDs, and the low rectifying properties of the cell due to the direct contact between the BP and Al cathode caused by the roughened surface of the active layer. In this study, we exchanged the oleic acid surface ligands for butylamine ligands to improve the electrical contact between the QDs and BP, and introduced a buffer layer consisting of PbSe QDs onto the composite layer (BP:QD) to avoid the direct contact between BP and the Al cathode. In addition, the QD buffer layer was treated with ethylenediamine to crosslink the PbSe QDs and increase the conductivity of the buffer layer.



### Reference:

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## Using novel approaches to nanoparticles and their assemblies

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New routes to nanoparticles and assemblies will be described and related to ideas concerning crystal growth. In particular the growth of columnar or rod like structures will be discussed in terms of kinetics and thermodynamics of crystal growth.

The interplay of various factors will be discussed and illustrated by the growth of lead selenide or sulphide and zinc oxide. Kinetic and thermodynamic factors affecting the growth of very small particles will be discussed in terms of numerical models.

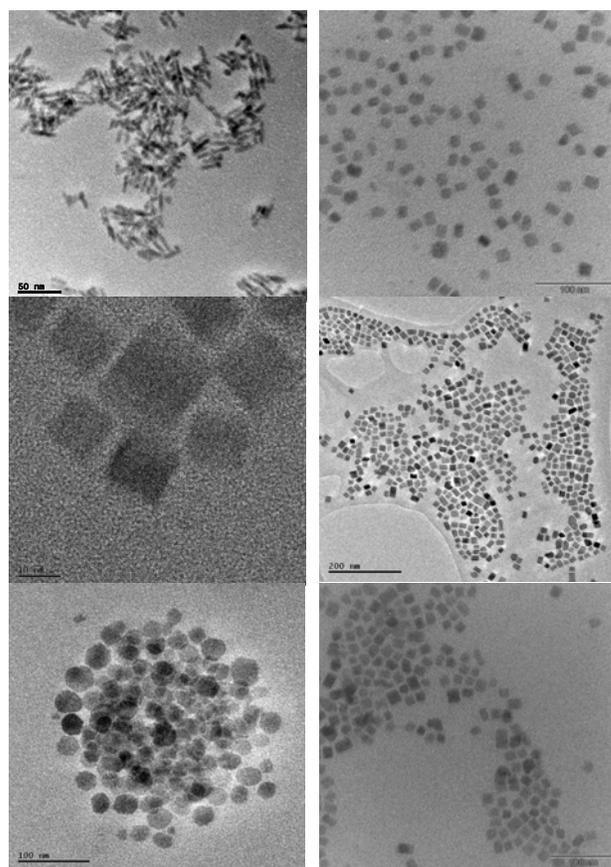


Figure 1. TEM image of PbSe nanoparticles prepared from PbCO<sub>3</sub> at left a) 190 °C b) 230 °C and c) 270 °C and right from Pb(NO<sub>3</sub>)<sub>2</sub> d) 190 °C e) 230 °C and f) 270 °C

## The health hazards of accidental exposure to nanoparticles

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This talk will discuss the general mechanisms of nanoparticle toxicity with respect to combustion-derived and manufactured nanoparticles (NP). Most human exposures so far concern combustion-derived NP but there has been a rapid increase in toxicology data concerning the potential hazard from manufacture NP. The most important portal of entry is the lungs although skin and gut are also portals of entry. I will cover nanoparticle toxicokinetics and the various extra-pulmonary targets that exist for inhaled nanoparticles. NP translocate from the lungs to the blood as a low fraction of the deposited dose and also gain access to the brain in a small

proportion of the deposited dose. The cardiovascular system is a target for combustion-derived nanoparticles and poses a likely target for manufactured NP. Our own research has shown that inhaled diesel NP have a profound adverse effect on the endothelium and clotting system in human subjects. Studies with the ApoE mice, that develop atherosclerotic plaques, has shown that diesel particle instillations stimulate increased plaque size. There is a need for structure-toxicity models in order to address the full range of nanoparticles that need tested. Finally I will describe some of our most recent data on the issue of fibre-shaped nanoparticles and the asbestos paradigm. Since being described in 1991 research and business communities have invested heavily in developing CNT for use in a wide range of products—often under the assumption that they are no more hazardous than graphite. The structure/activity paradigm underlying the pathogenicity of asbestos is well established, identifying the long rigid needle-like fibre shape and persistence in the lungs, as requirements for disease development and progression. Our research has shown that long, rigid multi-walled carbon nanotubes (MWCNT) show asbestos-like inflammatory behaviour in pleural and peritoneal mesothelial exposure model; in contrast, short and tangled MWCNT do not show such

behaviour (see Figure). Our results confirm that great caution is needed in introducing CNT products to market if a long-term legacy or harm is to be avoided, but that harmful asbestos-like behaviour can be prevented if nanotubes are manufactured with a short or tangled morphology.

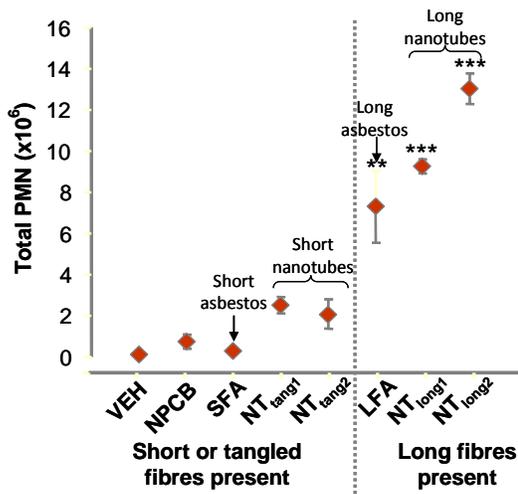


Figure 1.

Inflammatory effects, as PMN in peritoneal lavage, one day after injection of long CNT, long asbestos, short asbestos, short CNT and carbon black. Note that only long fibres caused inflammation.

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## Getting light and electrons across functionalised metal nanoparticles

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Nanoparticles are finding many new applications due to their unusual and tunable properties.<sup>1</sup> As size decreases, the metal core displays new properties that are absent in the bulk. An example of this is the appearance of a miscibility gap where none is observed for a bulk alloy. A clear example of this is the very recent observation of formation of core-shell structures during the synthesis of Au-Cu alloy nanoparticles for which a clear segregation of Au rich and Cu rich phases is observed in the nanometre size range.<sup>2</sup>

The advent of aberration corrected TEM equipment has allowed unprecedented material resolution, even for structures containing carbon and nitrogen atoms. An example of this is shown in Figure 1 for the imaging of a molecule of Galactose Oxidase to which a gold nanoparticle has been attached. This enzyme contains a Cu centre which can be specifically accessed through the ligand shell of a gold nanoparticle (Fig. 1).<sup>3</sup> An important consequence of using the ligand shell as a recognition centre is to allow facile electron transfer to a protein, where none is present on in the absence of recognition ligand.

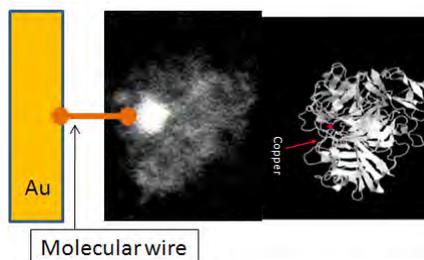


Figure 1.  
HAADF-STEM image of a redox enzyme coupled to a nanoparticle. Left: molecular model of the enzyme.<sup>2</sup>

The inclusion of recognition ligand in the stabilising shell of a nanoparticle can be used to self organise nanoparticles employing simple ideas from the chemistry of inorganic coordination compounds in order to achieve specificity for the construction of nanostructures<sup>4</sup> and for enhancing

electron transfer to redox centres.<sup>5</sup> The optical properties of nanoparticles can be greatly altered by proximity effects and by their geometry. This is of particular importance for practical applications in analytical chemistry, for example, for Surface Enhanced Raman Spectroscopy. The electrochemical synthesis of nanoparticles could

provide a new route for controlling geometry, since potential, and hence, rate of growth is determined by the applied potential. Although this approach is promising, there are, however still problem in obtaining stable reproducible preparations by the use of electrical potential modulation of the nucleation and growth steps.<sup>6</sup>

Reactivity and nanoparticle size has been the subject of many discussions and one of the problems has been how to prepare suitable nanoparticles establishing well defined contacts of nanoparticles of controlled size. Advances on this have been recently achieved<sup>7</sup> but surprisingly, a decrease in size does not necessarily lead to an increase in catalytic activity. These problems will be discussed during the presentation.

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