Biomagnetronics
Magnetic bacteria for biosensor applications

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The poster gives an overview of research being undertaken into the magnetic analysis and sorting of bacteria, which produce endogenous magnetic nanoparticles, so called magnetotactic bacteria.

Chemically synthesised magnetic nanoparticles are currently used experimentally for magnetic labelling of biological entities. One of the drawbacks of using these particles is their inhomogeneous size and moment distribution [1]. These inhomogeneities lead to a poor quantification of their detection response using current sensor technologies. The majority of these technologies are based upon the magnetoresistance (MR) effect such as the widely used tunneling MR (TMR) sensor [2].

The question arises whether or not magnetic nanoparticles naturally produced by magnetotactic bacteria have a more homogeneous particle distribution and therefore can be used to overcome this problem.

The first objective of our research was a thorough quantification of the magnetic properties and size distribution of endogenously produced magnetic nanoparticles in the bacteria. These characterisation studies included superconducting quantum interference device (SQUID) magnetometry and transmission electron microscopy (TEM) and provided detailed information on the magnetic moment, anisotropy strength and polydispersity of the endogenous Fe_3O_4 nanoparticle clusters inside the m*agnetospirillum sp.* bacteria.

We then describe and show the sorting of magnetotactic bacteria by means of a microfluidic channel with an externally applied magnetic field [3]. Ultimately a TMR sensor has been integrated into the microfluidic system for the purposes of magnetic analysis and selection of the magnetic bacteria (Fig. 1).

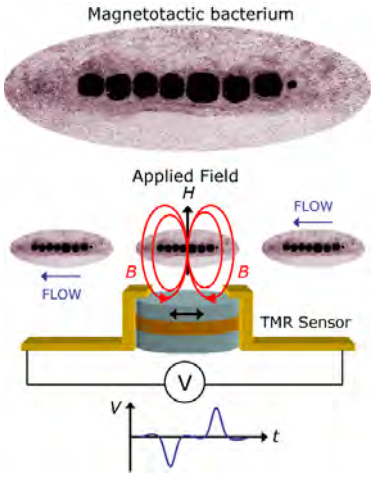

Figure 1. Schematic of the integrated sensor device in which a magnetotactic bacterium passes through a microchannel over a TMR sensor. This then detects the chain of endogenous superparamagnetic nanoparticles.

Reference:

[1] G. Micklem *et al.,* in *"Biomagnetism and Magnetic Biosystems Based on Molecular Recognition Processes",* edited by J.A.C. Bland and A. Ionescu, *AIP Conf. Proc.* 1025, Melville, New York, XIII (2008).

[2] D. L. Graham *et al*., *Trends in Biotechnology* 22, 455 (2004).

[3] K.S. Kim and J.-K. Park. *Lab Chip* 5, 1161 (2005).

Digital biomagnetism

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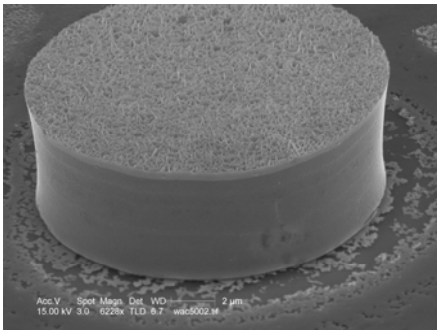
Microarrays and suspension-based assay technologies (SATs) have recently become common-place in biological laboratories for applications including genotyping, single nucleotide polymorphism (SNP) analysis and even simple separations or purifications. Microarrays have the capacity to test for thousands of targets in a single assay, whilst SATs benefit from flexibility and increased reaction kinetics associated with being a solution-phase technique.

Recently there has been demand for technologies that can offer both the flexibility of SATs and the ability to multiplex, necessitating that the individual microcarriers (beads) must be distinguishable from one-another. Most techniques aimed at achieving this rely heavily on optical encoding/identification of the microcarrier, be it by fluorescence or pattern recognition. All of these have inherent disadvantages, such as limitations on the number of possible codes or the need for complex and bulky optical recognition equipment. Current technologies also suffer from the need to make each distinguishable tag separately.

We are addressing these limitations by developing a magnetic-encoding technology, where multi-bit magnetic tags with magnetisations aligned in one of two distinct states allow for 2^N codes for an N bit tag. These tags all start nominally identical, thereby incorporating economy of scale and ease of manufacture. By modifying the coercivity of each bit a non-local field may be used to write any code to the tag. The tags are then released from the substrate, any reactions are performed and then they are sent across a magnetoresistive sensor embedded in a microfluidic channel for detection.

We show the fabrication of 3D electrodeposited multilayer pillar structures deposited from a single electrolytic bath. The bath contains salts of both magnetic (Ni/Co) and non-magnetic (Cu) metals, which are deposited in alternating layers by varying the applied potential. By controlling the concentration of additives in the electrolyte and the thickness/composition of each layer it is possible to coercivity-tune individual layers. A gold capping layer is then deposited to facilitate bio-functionalisation.

A bio-functionalisation scheme that exploits commercial microarray printing techniques to efficiently generate a vast library of probes will be described. A novel method for releasing the tags has also been produced based on an Al/Cu evaporated release layer that can be chemically dissolved without harming most biological entities. This allows tags functionalised with probe molecules by printing to be used within microfluidic systems for hybridisation, manipulation, and detection.



Reference:
[1] J. J. Palfreyman *et al.* “Digital biomagnetism: Electrodeposited multilayer magnetic barcodes” *Journal of Magnetism and Magnetic Materials*, 321, 10 (2009) p1662-1666.
[2] http://dx.doi.org/10.1016/j.jmmm.2009.02.109
[3] J.J Palfreyman *et al.* “Hybridization of Electrodeposited Magnetic Multilayer Micropillars” *IEEE Transactions on Magnetics*, 43, 6 (2007) p2439-2441.

A new technique for the surface area measurement of nanoparticles in liquid suspension

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Characterisation of nanoparticles is often difficult due to their active nature and limitations and requirements of particle sizing techniques. Surface area measurements are commonly used to characterise nanoparticles but these have usually been done in the dry state using traditional gas adsorption techniques. A new patented technique for measuring the surface area of nanoparticles whilst in liquid suspension has been developed based on NMR. Using the fact that the liquid in contact with the surface of the particle behaves differently from that of the bulk liquid, this effect can be detected through NMR relaxation and diffusion measurements. Xigo Nanotools have developed the Acorn Area based on this novel technology. The NMR based system offers the advantages of speed of analysis, with no sample preparation etc and can be used to high solids concentration. Comparisons with other techniques such as gas adsorption, DLS and titration are shown together examples of measurements on alumina, silica etc.

Synthesis of nanohydroxyapatite-chitosan composite using calcium phospor tris solution

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In this study, nanohydroxyapatite/chitosan composite has been synthesized through the process of precipitation where hydroxyapatite (HA) nanoparticles produced first time by using calcium phosphor tris (CaPTris) solution as a calcium phosphate medium as well as in the presence of simulated body fluid (SBF). Different amounts of HA and chitosan were used to produce nanohydroxyapatite/chitosan composite at 37 ^{o}C for 6 hours. The effect of HA nanoparticles/chitosan mass ratio (70-98 %) on nanocomposite formation was investigated at 0.4 % (w/v) chitosan/acetic acid constant ratio. The size distributions of HA nanoparticles synthesized from CaPTris were determined according to Dynamic Light Scattering method (ZetaSizer). Synthesized nanocomposite was also characterized in terms of structure (Fourier Transformed Infrared Spectrometry, FTIR, X-ray Diffractometry, XRD and Energy-dispersive X-ray Spectroscopy, EDX) and morphology (Scanning Electron Microscopy, SEM). XRD patterns of nanocomposite samples showed that density of HA peaks increased by increasing weight of HA in the formation of nanocomposite. SEM images of the samples exhibited that increased HA/chitosan mass ratio led to agglomeration of HA nanoparticles and best results were obtained at HA/chitosan mass ratio of 80-20 %. In that mass ratio, HA nanoparticles were less aggregated and precipitated on chitosan fiber. SEM images were also showed that nanocomposites had a porous structure which was beneficial for tissue in-growth. Ca/P ratios in the composites varied between 1.56-1.58. Characterization results depicted that HA/chitosan nanocomposite were also synthesized using CaPTris.

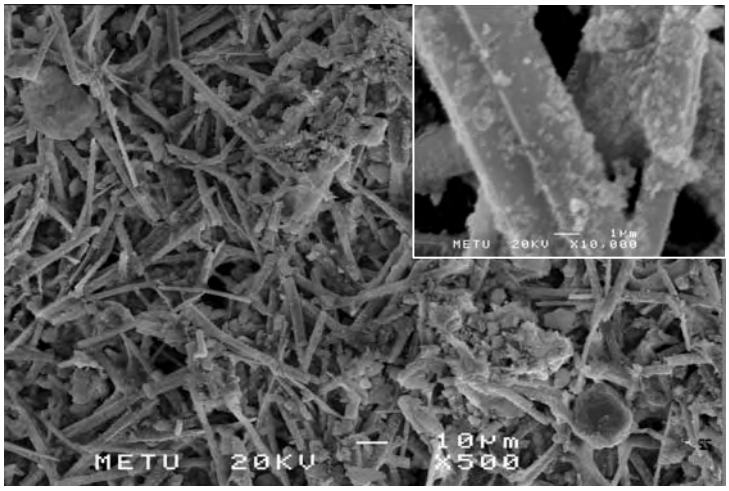

Figure 1. SEM image of HA/chitosan nanocomposite prepared at mass ratio of 80-20 %

Reference:
[1] “Synthesis and Characterization of Hydroxyapatite Nanoparticles”, Cengiz B., Gokce Y., Yildiz N., Aktas Z., Calimli A., Colloids and Surfaces A: Physicochemical and Engineering Aspects, 322, 2008, 29-33.
[2] “Synthesis of Calcium-Phosphate and Chitosan Bioceramics for Bone Regeneration”, Finisie, M.R., Josue, A., Favera, T., Laranjeira, M.C.M., *An. Acad. Bras. Cienc.*, 73 [4], 2001, 525-532.
[3] “Bioresorbable Composite Bone Paste Using Polysaccharide Based Nano Hydroxyapatite”, Murugan, R., Ramakrishna,S., Biomaterials, 25, 2004, 3829–3835.

Period four metal nanoparticles in combating biofouling & corrosion

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Biofouling and biocorrosion is ubiquitous wherever an aquatic environment exists, and is a resultant process of the agglomeration of bacteria upon a substrate. In order to prevent this, antimicrobial or biocidal compounds can be deposited into a substrate or surface coating in the form of active antimicrobial agents, such as nanoparticles [NP^S]. Metal NP^S (MNP^S) have been brought to attention as potential antimicrobial agents owing to the extensive research and knowledge that has already been formed from silver NP^S [1], that are already being doped into coatings in medical devices for use in combating infection [2].

Wet chemical methods have rendered a synthesis route for the preparation of MNP^S with tailored size and shape. One way of achieving this is using a synthetic step known as the 'polyol' process, where ethylene glycol serves as a solvent and joint reducing agent, and by elevating temperatures, growth of MNP^S can be achieved [3].

The research presented, shows how MNP^S can be synthesised through the polyol reduction method, with full characterisation achieved using analytical methods such as:

- UV-visible spectrophotometry (UV-vis), figure 1;
- Fluorescence;
- Particle Sizing;
- Field emission scanning electron microscopy (FESEM).

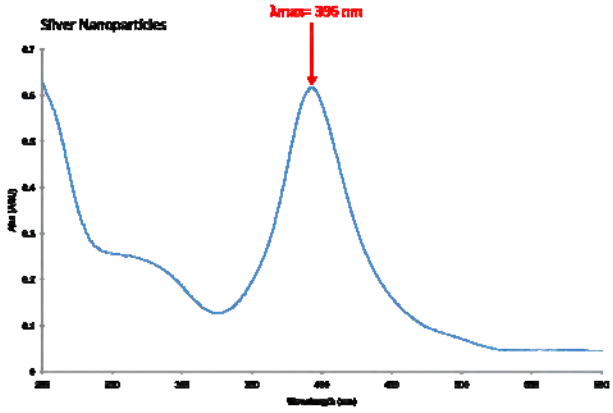

Figure 1: Showing silver nanoparticle absorption peak using UV-vis

The nanoparticles were incorporated into test materials and subjected to biofouling-based and biological test assays proving their efficacy in preventing biofouling. These results will be shown.

Reference:
[1] L.Joguet, I.Sondi and E.Matijevi J.Colloid Interface Sci. 251 (2002), P.284
[2] L.Bush, www.infectioncontroltoday.com (accessed 26th July 2009)
[3] I.Pastoriza and L.Liz-Marzan Adv, Func, Mat. 19 (2009) P679-688

Nanoparticle based antifouling materials for environmental sensing technologies

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For marine and riverine sensors, biofouling decreases the operating lifetime and increases the cost of maintenance of a submerged device [1,2]. A solution to prevent biofilm formation is the development of novel antifouling materials that can be applied to a sensor housing or windows to combat these deleterious effects. The use of antibacterial agents incorporated into polymers is proposed with the objective of conferring antifouling ability to polymer-coated surfaces.

Metal nanoparticles are known to exhibit many properties and antibacterial ability is just one such quality that some metal nanoparticles possess [3]. Therefore, the inclusion of nanoparticles into polymers offers a solution to environmental biofilm accumulation. In this study, it has been demonstrated that metal nanoparticles incorporated into poly (vinyl chloride) (PVC) display a noticeable decrease in bacterial adhesion compared to the PVC control. This follows exposure of the doped polymer surfaces to *Staphylococcus aureus* and *Escherichia coli* for a set period of time and observation of the adhered cells by epifluorescence microscopy. Results of the biological analysis and imaging studies will be presented.

Figure 1

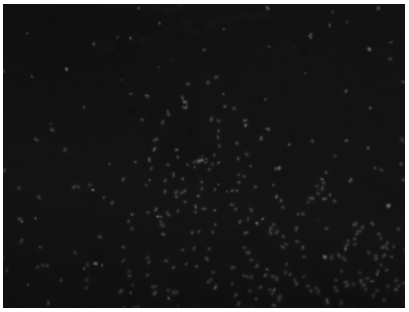

Figure 1 (left): Unmodified PVC control following exposure to *E. coli* cells for one hour.

Figure 2

Figure 2 (right): PVC doped with TiO_2 nanoparticles following exposure to *E. coli* cells for one hour.

Reference:
[1] M. J. Smith, G. Adam, H. J. Duncan and M. J. Cowling, *Estuarine, Coastal and Shelf Science*, 2002, 55, 361–367.
[2] S. J. Marrs, R.M. Head, M. J. Cowling, T. Hodgekiess and J. Davenport, *Estuarine, Coastal and Shelf Science*, 1999, 48, 137–141.
[3] E. Weir, A. Lawlor, A. Whelan and F. Regan, *Analyst*, 2008, *133*, 835–845.

Development of nanomaterials that can be used to track stem cells

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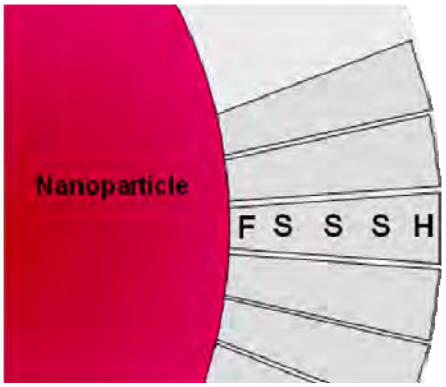
Tracking stem cells *in vivo* is a prerequisite to stem cell therapies gaining regulatory approval. One method of tracking is to label cells with MRI contrast enhancing agents, like superparamagnetic iron oxide nanoparticles (SPIONs).

To use nanoparticles in biological applications, they need to be coated by a ligand shell (called biofunctionalisation) to provide stability in a physiological environment, including preventing non-specific binding, and to facilitate internalisation and retention in the stem cell. The ligand shell usually consists of a self-assembled monolayer of ligand consisting of a 'head', 'stem' and 'foot'. The 'foot' and 'stem' drive self-assembly of the shell and seal off the core material from the environment. The environment is only exposed to the 'head' and the distal end of the 'stem'. While the 'stem' and 'head' groups can be easily transposed to many different kinds of nanoparticles, the 'foot' must be adapted according to the surface properties of the nanoparticle.

Quantum dots are easier to quantify than SPIONs due to their fluorescent properties and have therefore been used to screen different ligand shells. A novel protocol, using PEG alkanethiol ligands to biofunctionalise quantum dots, has been developed. These PEG-capped quantum dots are highly stable and soluble in physiological conditions according to a series of stability tests of increasing stringency. Crucially, they do not exhibit non-specific binding to cells and a controlled number of a specific recognition function can be introduced within the shell for targeting [1]. First, these nanomaterials, which are resistant to photobleaching, will be used in live cell imaging. The ligand shell technology will then be transposed to SPIONs to allow *in vivo* imaging and tracking of stem cells, by the simple means of adapting the thiol 'foot' to SPION materials.



Schematic representation of a ligand shell coating and protecting a nanoparticle from the surrounding environment.

F = foot (anchoring to the nanoparticle)

S = stem (hydrophobic interactions/hydrogen bonding)

H = head (uncharged polar extremity for solubility)

Reference:
[1] "A Generic Approach to Monofunctionalised Protein-Like Gold Nanoparticles Based on Immobilised Metal Ion Affinity Chromatography." R. Levy, Z. Wang, L. Duchesne, R.C. Doty, A.I. Cooper, M. Brust & D.G. Fernig, ChemBioChem, 7[4], 2006, 592-594.

Utilisation of DFGF for the separation and purification of gold nanoparticles.

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Electroseparation methods have long been required and developed, but with the complexity of ITP, the sample limitations of CE and the mobile phase and support problems in CEC, HPLC is still the major liquid separation technique, despite the major problems and limitations associated with this technique.

However, research has continued on the combined development of these electrophoretic techniques by combining the new developments of microfabrication, detection, computer control of fluidics and voltages new electrophoretic techniques immerged that removes all the disadvantages of the individual techniques.

DFGF, (Dynamic Field Gradient Focusing), is a new separation technique which exploits the differences in electrophoretic mobility of analytes to result in a separation. This is achieved by taking a channel and applying a hydrodynamic flow in one direction and a counteracting electric field gradient acting in the opposite direction. This results in analytes reaching a focal point according to their electrophoretic mobility.

As GNP's have different charges dependant on size, recent work by the Chromatography group has seen the purification of GNP's from aggregates. This ground breaking separation is shown in figure 1. Work in progress aims to see the separation of a mixture of GNPs with particle size distributions of 10nm and 14nm. As GNP's are difficult to separate[1] this technique provides a chromatographic method which will separate the particles and unlike other chromatographic techniques, will not dilute sample as DFGF can also adjust and optimise peak mass and concentration to a given detection system, so that trace analytes can be detected and analysed in the presence of bulk analytes.

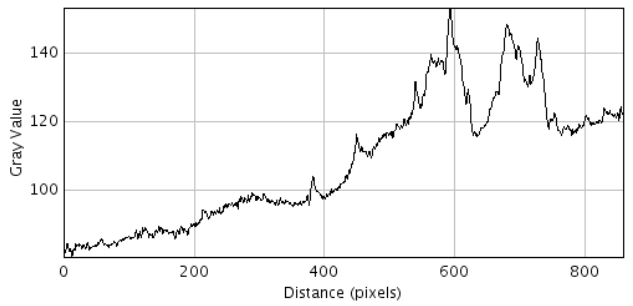

Figure 1. Image of the separation channel of the DFGF device with the GNP's separated from the aggregates.

Reference:
[1] Private communication Professor M Brust University of Liverpool

Nanoparticle-modified polymer capsules as multifunctional systems for biosensing and drug delivery applications

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One of the possible contributions of nanomedicine consists in building biocompatible multifunctional carrier systems that are able to navigate within living organisms using remote guidance and activation for the local release of their cargo. Such carrier systems can be used to improve cargo stability, to sustain and control their release rates, to increase the bioavailability of cargo substances, and to target them to specific sites within the body.

Multilayer polyelectrolyte capsules are spherical microcontainers based on layer-by-layer adsorption of oppositely charged polyelectrolyte polymers onto a sacrificial template followed by the decomposition of this template. Compared to other systems (such as liposomes, block copolymers, and dendrimer polymers) polymer capsules have many advantageous properties which make them attractive candidates for medical applications including biosensing and drug delivery. Firstly, they can be synthesized under mild conditions by using numerous different materials. Secondly, their functional properties can be well-defined by embedding different nanoscale building blocks (as colloidal inorganic nanoparticles or biomolecules) within and on top of their wall. Thirdly, they can efficiently host (biological) macromolecules within their cavity for numerous biomedical applications. Finally, they can be composed of biocompatible materials for the delivery of encapsulated materials into cells [1].

In this work the main concepts concerning the fabrication of polyelectrolyte capsules based on calcium carbonate cores are described and their applications for delivery and sensing in cells are showed. The use of these systems is envisioned to open new ways in a broad range of disciplines since their properties may be promptly tailored to specific applications by varying the nature of the encapsulated material and the polymer shell composition.

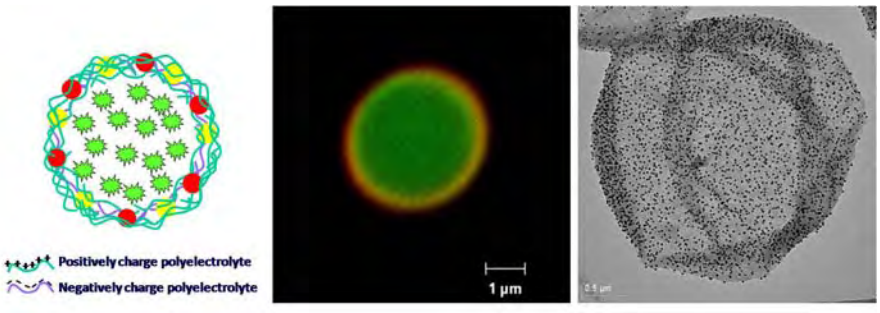

Figure 1. Nanoparticle-modified polymer capsule. (Left) Geometry of polymer capsule loaded with fluorescent (red), and gold (yellow) NPs in the wall and filled with cargo molecules (green star-shape). (Center) Laser scanning confocal microscope image showing a single capsule loaded with green-fluorescent dextran into the cavity and red-emitting nanoparticles into the wall. (Right) Transmission Electron Microscope image showing a single capsule containing Au nanoparticles embedded into the polyelectrolyte shell.

Reference:

[1] Rivera G. P., del Mercato L. L., del Pino P., Munoz J. A., Parak W. J. “Nanoparticle modified polyelectrolyte capsules”, Nano Today, 3, 12-21, 2008.

Ion and pH sensing with colloidal nanoparticles - the influence of surface charge on sensing and colloidal properties

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Ion sensitive colloidal nanoparticles are typically charged in order to be colloidally stable. By linking pH sensitive fluorescence dye, SNARF, to amphiphilic polymer coated gold nanoparticles, we demonstrate that this charge can significantly change the binding constant of the ions to the nanoparticles and thus change the read-out. The sensor read-out is not determined by the ion concentration in the bulk, but by the ion concentration in the local nano-environment of the nanoparticles. In the case of SNARF conjugated gold nanoparticles, the pK_a of SNARF molecule shifts to higher values with the negatively charged particle surface. By using longer crosslinkers to be the spacers between SNARF and negatively charged gold nanoparticles, we can control the pH sensitivity of SNARF modified gold nanoparticles between neutral and basic pH range.

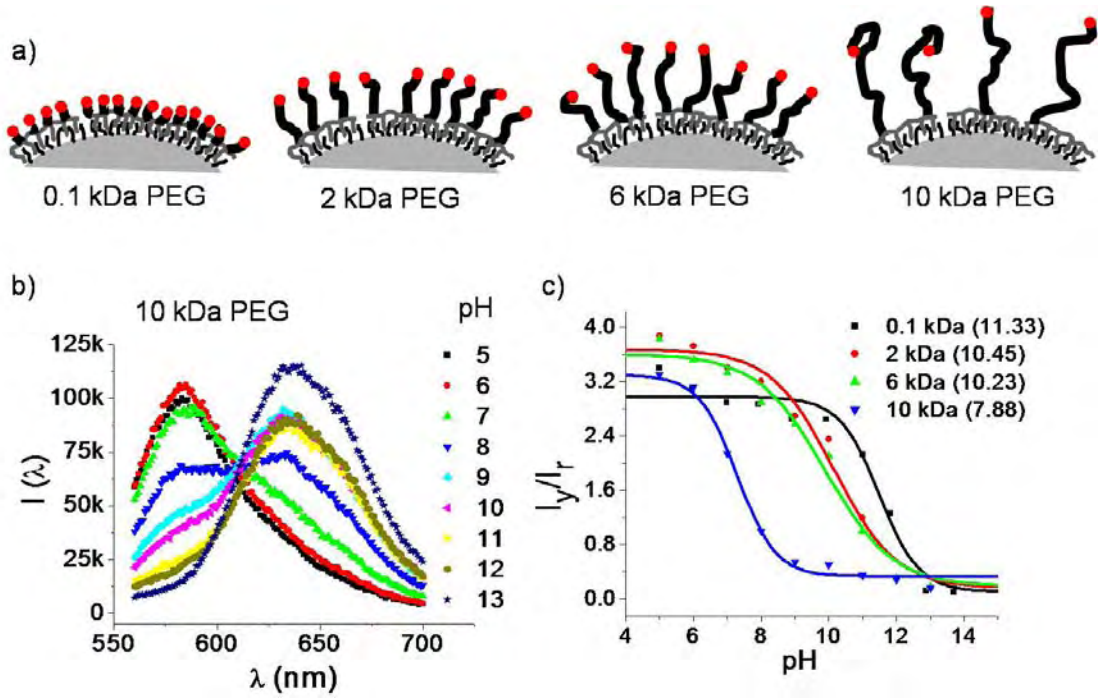

Figure. a) SNARF molecules (drawn in red) conjugated to PEG molecules of different molecular weight were linked to the surface of polymer-coated gold nanoparticles. The negatively charged polymer and surfactant layer forms an additional spacer between the Au cores and the PEG ligands. The sketches have to be understood as plausible idealized model for the conformation of the conjugates and are not drawn to scale. b) Fluorescence spectra I(λ) of polymer-coated Au nanoparticles with attached SNARF / 10 kDa PEG molecules. The particles were solubilized in buffers with different pH. The samples were excited with 540 nm. c) For each sample and each pH value the ratio I_y/I_r of the fluorescence intensities I(587nm)/I(641nm) was derived from the respective fluorescence spectrum. I_y/I_r versus pH curves are shown for the four different samples. Here pH refers to the bulk pH. Each of the curves was fitted with a sigmoidal function. The pK_a values of samples are indicated in the brackets.

1D metal oxide nanowires by hydrothermal synthesis

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Firstly, using a standard hydrothermal synthesis technique, we have specifically focused on the production and dimensional control of different 1-dimensional transition metal oxide nanowires, including WO_x (x=2-3) and Fe_2O_3 nanowires. In particular, the resulting ultrathin WO_x nanowires exhibited a very high specific surface area, >150 m_2/g. Secondly, the investigation was extended further to apply the WO_x nanowires as a template, to synthesise a new type of tungsten nitride nanowires, via a nitriding process. Finally, using a modified hydrothermal reaction vessel which allows for superfast freezing the intermediate nanoparticles formed during the hydrothermal process, preliminarily experiments were carried out to investigate the progression and evolution of the nanomaterials inside the high temperature high pressure reaction vessel. Assisted with combined high resolution transmission electron microscope and energy dispersive x-ray spectrum analyses, the intermediate phase/structure for nanowire growth can be identified, which could shed light on the understanding of the fundamental nanomaterials science. As an example, it is confirmed that rod-like FeO(OH) has been the primary intermediate phase for the formation of Fe_2O_3 nanorods, and the aggregation and re-organisation of many quasi-crystalline clusters of Fe_2O_3 on a bigger Fe_2O_3 template lead to the growth of single crystalline Fe_2O_3 nanorods.

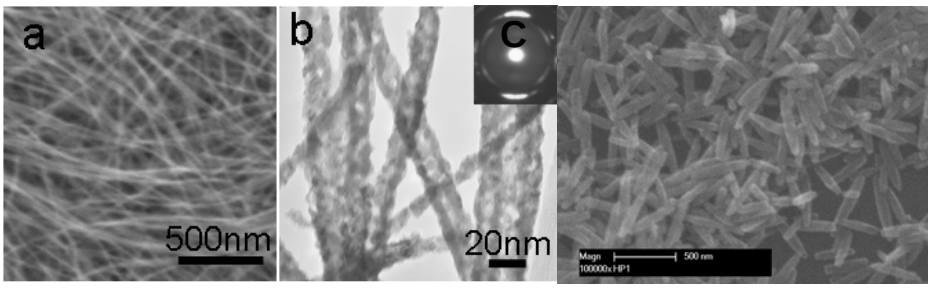

Figure 1. (a) Bundles of tungsten oxide nanowires synthesized by hydrothermal; (b) Tungsten nitride nanowires converted using the tungsten oxide bundles; and (c) Fe_2O_3 nanorods synthesized by the hydrothermal process.

Spherical carbon nanostructures

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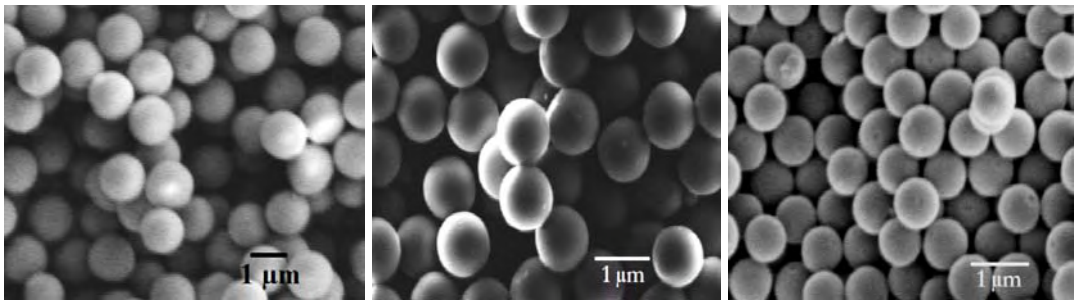
We present a synthetic route towards monodisperse smooth carbon nanospheres via the preparation and subsequent pyrolyis of spherical melamine formaldehyde copolymer microparticles[1]. By varying the reaction parameters the diameter of the initial copolymer particles and hence the diameter of the carbon spheres could be adjusted between several tens to several hundreds of nanometers for the carbon particles. Due to the loss of nitrogen and oxygen compounds in the process of carbonization the spheres pass strong shrinking to a final diameter that only measures 20% of the MF-spheres diameter. Despite this shrinkage they are still spherical particles that meet the high quality standards of common prepared and used polymer or silica spheres and are therefore a promising material with great potential.

These properties are key criteria's for their use as photonic band gap material. Synthetic opals were build from carbon spheres via sonic-supported sedimentation and were subsequently analyzed towards their optical properties. The crystals show a photonic band gap in the infrared region. Another approach in the production of photonic crystals may be to use such a carbon opal as a template for an inverse opal due to their high thermal resistance under non-oxidizing conditions.

The structure of spheres has been studied during different stages of carbonization by scanning electron microscopy, nuclear magnetic resonance and Fourier transform infrared spectroscopy. The properties of the carbon opals were determined using scanning electron microscopy, Fourier transform infrared spectroscopy and current-voltage measurements.



MF Spheres ... as-synthesized ...pyrolyzed at 400°C ...carbonized at 1000°C

Reference:
[1] " Preparation of Monodisperse, Submicrometer Carbon Spheres by Pyrolysis of Melamine-Formaldehyde Resin", B. Friedel, S. Greulich-Weber, Small, 2[7], 2006, 859-863.

Synthesis, Stabilization and Functionalization of Triangular Silver Nanoprisms

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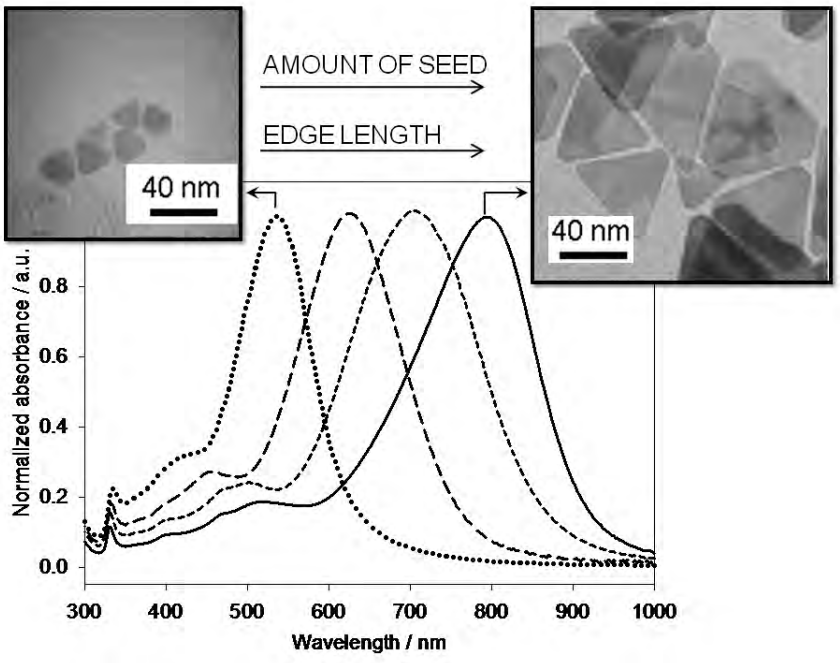
Details are presented of a rapid, room temperature synthesis of silver nanoprisms. This is a seeded process and requires only aqueous solvent. The product particles exhibit a uniform tabular triangular morphology and a narrow size distribution. The edge-length of the prisms is determined by the concentration of seed particles, which in turn offers tuneable control over the spectral position of the surface plasmon resonance (SPR) band. Furthermore, discrete dipole approximation (DDA) calculations predict that the localized electric field enhancement at the SPR is much greater for triangular nanoplates relative to isotropic spherical nanoparticles. Owing to these characteristic properties, Ag nanoprisms possess significant potentiality for varied applications including antibody-antigen assays, surface enhanced Raman spectroscopy (SERS) and metal enhanced fluorescence (MEF).

A particular challenge to the utilisation of triangular Ag nanoprisms in bioassays, is their lack of stability in the presence of halides, thereby rendering unfeasible, the direct use of the particles in salt solution. We have developed various methodologies to circumvent this problem. Outlined here are the details of the functionalization of the silver particles by silica (SiO_2) and titania (TiO_2) coating procedures. In addition to conferring enhanced stability to the nanoprisms in salt solution, these approaches facilitate the conjugation of bio-molecules, through well developed silica and titania coordination chemistry.



Reference:
[1] "Optical Properties and Growth Aspects of Silver Nanoprisms Produced by a Highly Reproducible and Rapid Synthesis at Room Temperature", D. Aherne, D.M. Ledwith, M Gara and J.M. Kelly, Adv. Funct. Mater. [18], 2008, 2005-2016.
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CdSe and CdSe/CdS Nanoparticles from Single Molecular Precursors in Microfluidic Reactor

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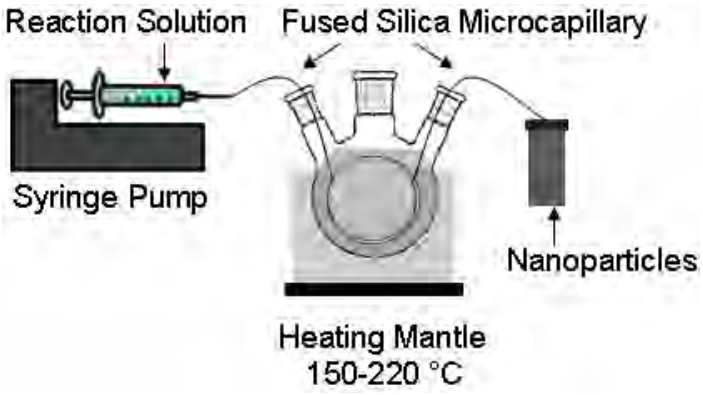
Microfluidic reactor with fused silica capillaries acting as the reaction channels has been utilized for the continuous synthesis of highly luminescent CdSe (core) and CdSe/CdS (core/shell) nanoparticles from single molecular precursors. Synthesis of CdSe nanoparticles was carried out from a selenophosphinate compound; $[Cd(^{i}Pr_2PSe_2)_2]$[1]. Resulting crude CdSe nanoparticles were mixed with $[Cd(S_2CNMe^{n}Hex)_2]$[2] and injected back into the capillary to form the CdS-coated CdSe nanoparticles. Size, shell thickness and consequently quantum yield were controlled by temperature, residence time or precursors concentration. The nanoparticles were charactrized by UV-visible spectroscopy, photoluminescence, X-ray diffraction analysis and transmission electron microscopy.



Reference:
[1] "Metal complexes of selenophosphinates from reactions with $(R_2PSe)_2Se$: $[M(R_2PSe_2)_n]$ (M = Zn^{II}, Cd^{II}, Pb^{II}, In^{III}, Ga^{III}, Cu^{I}, Bi^{III}, Ni^{II}; R = ^{i}Pr, Ph) and $[Mo^{V}_2O_2Se_2(Se_2P^{i}Pr_2)_2]$"
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