

Synthesis and characterization of semiconductor nanoparticle-carbon-nanotube composites in terms of their application in hybrid solar cells

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The dynamic progress in the field of nanotechnology affords an approach to several physical and chemical challenges from the very bottom. Light absorption and effective charge separation in organic solar cells provide such problems rendering purely organic devices uncompetitive compared to conventional silicon solar cells. The integration of novel semiconductor nanoparticle-carbon-nanotube composites into organic structures is expected to significantly improve the device performance. Due to quantum confinement, semiconductor nanoparticles (NPs) can act as tunable light absorbers while carbon nanotubes (CNTs) are considered as supporting material for quantum dots as well as charge (transport) medium since the CNTs reveal mechanical stability, chemical inertness and provide ballistic transport. In contrast to the common methods of NP attachment to CNTs which degrade their outstanding properties, we present a "one pot" synthesis for NP-CNT composites under benign conditions. Assuming close interaction of the CNT π -system with the individual particle, a gapless interface is created as promising charge separation site. Composite materials based on semiconducting NPs with different bandgaps are presented. The investigations of optoelectronic properties were carried out on a single NP-CNT as well as on networks embedded into conducting polymer. The increase in conductivity by up to three orders of magnitude provided by a single nanotube covered with quantum dots indicates high potential of proposed structures.

The influence of the unfunctionalized CNTs on the synthesis of semiconducting NPs and an attachment mechanism will be discussed. This will be supported by microscopical and spectroscopical characterizations, transport and photoconductivity measurements.

The presented noncovalent attachment of NPs to CNTs combines the unique possibility of band gap tuning of semiconducting quantum dots with the excellent conductivity of one dimensional systems such as carbon nanotubes. Therefore, we expect a large impact of these materials in optoelectronics and especially in photovoltaics.

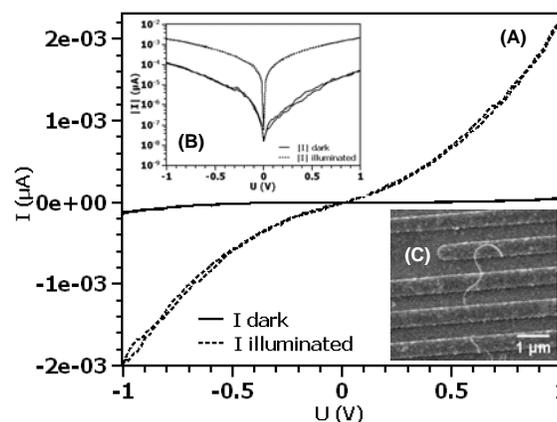


Figure 1: (A) linear and (B) semilogarithmic IV-plot (C) of one NP-CNT presented in the SEM picture.

Reference:

- [1] B. H. Juárez, C. Klinke, A. Kornowski, and H. Weller, *Nano Letters*, 7 [12], 2007, 3564-3568.
- [2] A. B. Hungría, B. H. Juárez, C. Klinke, H. Weller, and P. A. Midgley, *Nano Research*, 1, 2008, 89-97.
- [3] B. H. Juárez, M. Meyns, A. Chanaewa, Y. Cai, C. Klinke, and H. Weller, *J. Am. Chem. Soc.*, 130 [46], 2008, 15282-15284.

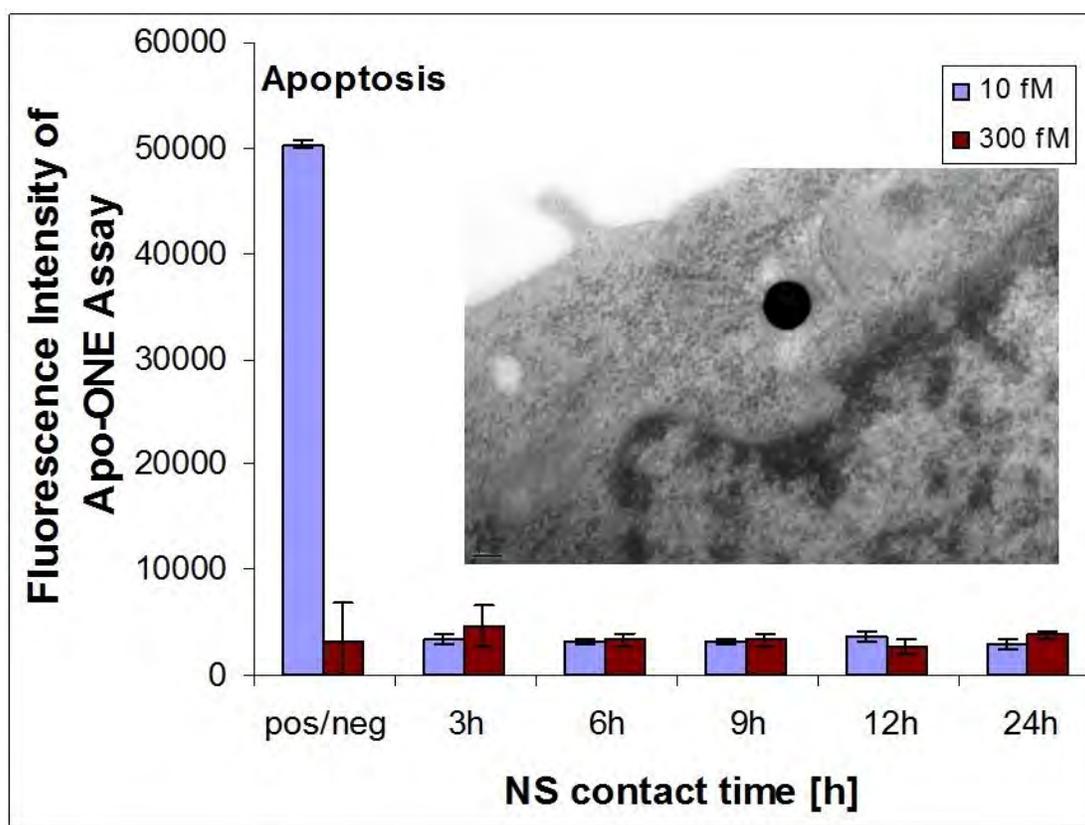
Nanoshells for surface enhanced Raman spectroscopy in eucaryotic cells: cellular response and sensor development

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We have investigated the use of gold nanoshells (NS) as a Surface enhanced Raman (SER) platform for intracellular sensing in eucaryotic cells using a near infrared Raman system. To show the feasibility of using these 151 ± 5 nm sized solution-stable nanoparticles inside living cells we investigated the uptake, cellular response and the health of the cell population. We found that NS are taken up voluntarily and can be found in the cytosol by transmission electron microscopy (TEM) which also provides detailed information about location and immediate surrounding of the NS. The internalization into cells has been found to be independent of active cellular mechanisms like endocytosis. Uptake of NS into cells can be controlled and cells show no increase in necrosis or apoptosis as determined by the measurement of specific molecular markers. We show that NS based intra-cytosolic SERS can be measured on biological samples using short acquisition times and low laser powers. In addition we have developed these sensors for measurement of a variety of cellular conditions such as pH, redox potential and the concentration of specific proteins.



Characterization of proteins adsorbed on AuNPs in different cell culture media: the role of protein corona in the cellular response

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Due to their very small dimensions (sub-100 nm), nanoparticles (NPs) show fascinating physicochemical properties, unlike corresponding bulk materials, leading to their wide use in many industrial applications worldwide. However, a certain anxiety about their potential impact on human health was recently recognized, especially concerning the mechanisms underlying NPs interactions with biological systems (risk assessment and definition of hazards). When NPs enter a biological fluid, proteins interchange onto NPs surface area, resulting in the formation of dynamic new “bio-nano entities”. Such hybrid bionanostructures (protein corona-coated NPs) may have a crucial role in determining the biological responses and their fate. Since protein NPs coatings may vary as a function of several parameters such as incubation time, NPs and suspending media properties, in this work we aimed at developing a methodological approach to characterize the protein corona of gold NPs of different sizes, upon their reaction with several cell culture media, and its temporal evolution. Citrate-capped AuNPs were deeply characterized in terms of size, shape, surface characteristics, long-term stability and purity by means of Dynamic Light Scattering, UV-Vis spectra, SEM, TEM, AFM, agarose gel electrophoresis. Afterwards, we evaluated the dynamic formation of protein corona by applying the above mentioned techniques along with SDS-PAGE and mass spectrometry, at different elapsed time of incubation. Results show that the different composition of cells media strongly affect the proteins corona formation, with a role ascribable to size, shape and surface area of NPs (see figure). In order to evaluate the potential biological impact of such hybrid bio-nanostructures, we incubated them with several cells line, studying NPs uptake, distribution and clearance in living cells, as well as the subsequent biological response in terms of nanotoxicity with several advanced characterization techniques, such as 2-photon confocal microscopy of unlabeled AuNPs and proteomic analyses (DIGE).

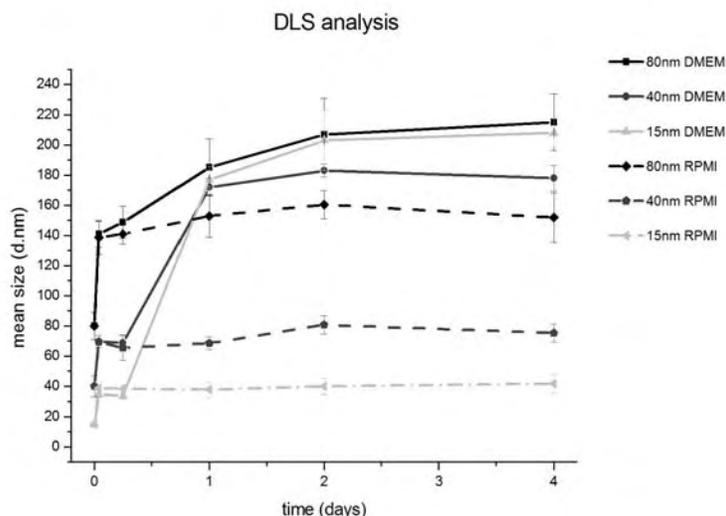


Figure 1. DLS analysis in time (days) of 15nm, 40nm and 80nm AuNPs in DMEM and RPMI cell culture media plus Fetal Bovine Serum (FBS) 10%. Each size of AuNPs probed was incubated at a concentration giving the same total surface area.

The biological implications of radiation induced photoelectron production, as a function of particle size and composition

C. V. Howard, A. Elsaesser & C. Busby
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The toxicity of heavy metals in biological systems is not fully understood. We posit that the interaction between high atomic number elements and background radiation could be significant, by inducing oxidative stress, through photoelectron generation, by the mechanism of ionisation of water into reactive oxygen species (ROS). Ambient nanoparticles can gain entry to the body through various portals [1].

It is noteworthy that element in our natural biochemistry with the highest atomic number (Z) is iodine and that the thyroid gland, where most of the iodine is sequestered, is the most radiosensitive gland in the body. That evolution has shunned the incorporation of higher Z elements into biochemistry must prompt the question why?

For low keV primary photons, the level of photo-electron production is proportional to the 5th power of the atomic number [2]. We have modelled the effect of particle size on the bioavailability of secondary photo-electrons. For keV photoelectrons the escape depth from metals is of the order 5 nm (Huefner, 1996). As particle size decreases, internal absorption decreases and the proportion available to 'escape' into surrounding tissues increases. Monte Carlo simulations show that for particle sizes below 10 nm this effect plateaus and most secondary photoelectrons generated escape from the particle.

These "free" electrons have the ability to produce reactive oxygen species, a key player in cellular cyto- and genotoxicity. Counter-intuitively it is lower energy radiation, in the eV and low keV range, that will cause the most biological damage because low energy photoelectrons will have the highest ionisation density along their tracks while within the body [4]. The likely biological and pathological sequelae will be discussed.

Reference:

- [1] The potential risks of nanomaterials: a review carried out for ECETOC. Borm PJ, Robbins D, Haubold S, Kuhlbusch T, Fissan H, Donaldson K, Schins R, Stone V, Kreyling W, Lademann J, Krutmann J, Warheit D and Oberdorster E. *Particle and Fibre Toxicology*. 14,, 2006;3:11.
- [2] Ueber einen die Erzeugung und Verwandlung des Lichtes betreffenden heuristischen Gesichtspunkt. Einstein A, *Annalen der Physik* 6, 1905, 132-148.
- [3] Photoelectron Spectroscopy: principles and applications. S Huefner, 1996,, Springer, Berlin.
- [4] Does Uranium contamination amplify natural background radiation dose to the D.A? Busby C *Eur. J. Biol. Biolmagn.* 1 (2), 2005, 120-131.

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- [2] Ueber einen die Erzeugung und Verwandlung des Lichtes betreffenden heuristischen Gesichtspunkt. Einstein A, *Annalen der Physik* 6, 1905, 132-148.
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- [4] Does Uranium contamination amplify natural background radiation dose to the D.A? Busby C *Eur. J. Biol. Biolmagn.* 1 (2), 2005, 120-131.

The suitability of commercial nanoparticles for magnetic hyperthermia therapy

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There is an obvious and widespread need for an alternative treatment of metastatic cancer that does not rely upon systemic therapies such as chemotherapy or radiotherapy, which can result in adverse side effects. In treating cancer cells, there is often damage sustained to healthy cells inducing increased strain on an already weakened body.

One viable solution would be to develop a specific localised treatment that would deliver biomolecular therapeutic agents, preferentially targeting cancer cells, that could then be activated in a controlled manner thus increasing the efficiency of the therapy where needed. One particular method relies upon heat generated from a magnetic nanoparticle under the influence of an externally applied alternating magnetic field. This method, known as magnetic hyperthermia, is ideally suited for treating metastatic cancers which are highly susceptible to cell death as a response to a small increase in local temperature, typically between 3-5°C [1].

It is crucial to study the calorimetric efficiency of nanoparticles to optimise them for hyperthermic treatment. Commercial nanoparticles from Chemicell, Micromod and Bayer-Schering were characterised on hydrodynamic diameter, total iron content and relative ferrous iron content and crystalline diameter [2]. Additionally calorimetric measurements were taken using a 900 kHz AC magnetic field of 3 kA/m.

Our findings conclude that 4 out of the 16 samples containing relatively high (>18%) ferrous content on average generate an intrinsic loss power (ILP, a system-independent parameter) of less than 12% compared to other particles. Highest ILP 3.1 nHm²/kg) was achieved for particles with hydrodynamic diameter of around 70 nm and crystallite diameter of 12 nm.

To complement these studies a small in-vivo murine study (n=11) was performed using commercial nanoparticles with a high ILP. The effectiveness of magnetic hyperthermia on subcutaneous tumours (Breast cancer cell line MDA-MB231) is discussed with particular emphasis on cell viability as a function of local heating rates as shown in Figure 1.

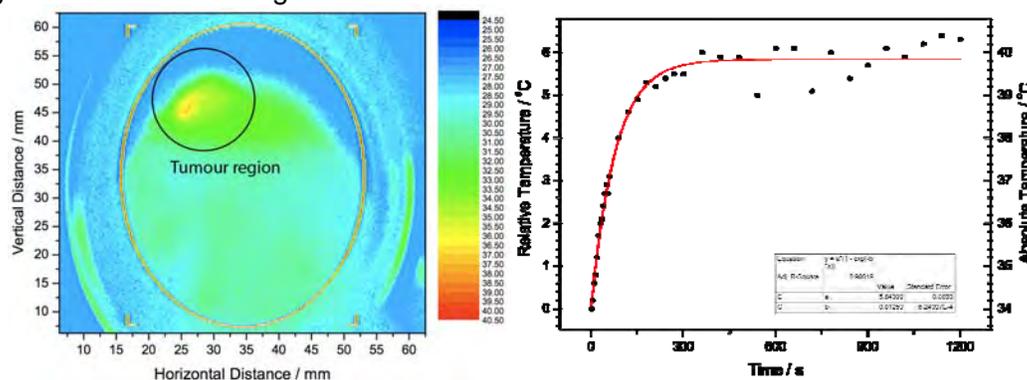


Figure 1. Surface heat map across tumour region (left) and associated temperature profile during exposure to an alternating magnetic field (right).

Reference:

[1] Pankhurst, Q.A., et al., *Applications of magnetic nanoparticles in biomedicine*. Journal of Physics D-Applied Physics, 2003. 36(13): p. R167-R181.

[2] Kallumadil, M., et al., *Suitability of commercial colloids for magnetic hyperthermia*. Journal of Magnetism and Magnetic Materials, 2009. 321: p. 1509-1513.

Fabrication of photo-induced patterned conducting polymer films containing gold nanoparticles

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Novel multifunctional nanocomposite, conducting polymer poly(thiophene) coated gold nanoparticles including cinnamate moiety (P3OT-AuNPs-CI), is newly developed. The cinnamate moiety, which is well-known for its photoreactive properties, causes aggregation of the AuNPs by means of UV irradiation. We can obtain patterned P3OT-AuNPs-CI thin film using this fast and easy UV irradiation system. This new nanocomposite provides a convenient patterning technique, which can alternate the conventional lithography on the patterning process of conducting polymer, as well as sufficient conductivity for sub-micro and microscale electronic devices. We suggest that this new multifunctional nanomaterial can be applied to manufacture microelectronic devices and circuits, solar cells, diode, and chemical sensor.

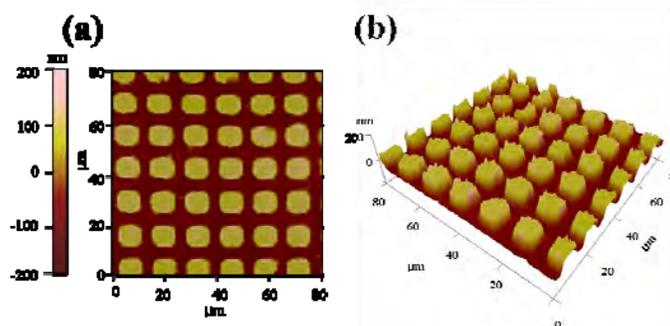


Figure 1. AFM images of the 7.5 μm P3OT-AuNPs-CI pattern: (a) Two-dimensional (2D) and (b) three dimensional (3D) surface morphologies. The height is about 100 nm.

Reference:

[1] "Polyaniline Nanofiber/Gold Nanoparticle Nonvolatile Memory", Tseng, R. J.; Huang, J.; Ouyang, J.; Richard B. Kaner, R. B.; Yang, Y. *Nano Lett.* 2005, 5, 1077-1080.

[2] "Formation of Patterned Microstructures of Conducting Polymers by Soft Lithography, and Applications in Microelectronic Device Fabrication", Beh, W.S.; Kim, I. T.; Qin, D.; Xia, Y.; Whitesides, G. M., *Adv. Mater.* 1999, 11, 1038-1041.

Stimulus-Responsive Liquid Marbles¹

Damien Dupin, Steven P. Armes and Syuji Fujii[†]*

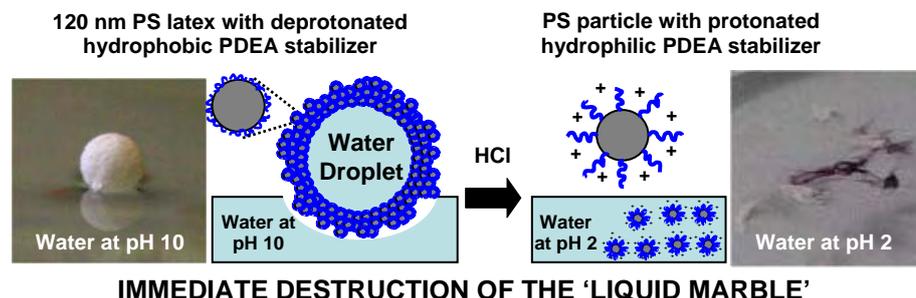
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Millimeter-sized 'liquid marbles' are usually prepared using highly hydrophobic particles such as fluorosilane-treated lycopodium powder or alkylated silica sols. In the present work it is shown that 'liquid marbles' can be prepared using sterically-stabilized polystyrene latex; remarkably, such latex particles can be readily prepared by *aqueous emulsion* polymerization using a well-defined styrene-functionalized poly(2-(diethylamino)ethyl methacrylate) macromonomer as a reactive steric stabilizer. The macromonomer stabilizer chains are water-soluble when partially protonated below their pK_a of around 7.0, but become sufficiently hydrophobic in their deprotonated form to allow formation of robust 'liquid marbles' that remain stable when placed at the air/water interface. Moreover, the stabilizer chains confer pH-responsive behavior on the 'liquid marbles'; addition of acid to the aqueous sub-phase causes immediate destruction of the 'liquid marble'. Finally, a water-soluble dye is used to demonstrate payload release, which suggests potential encapsulation applications.



Reference:

[1] Dupin, D.; Fujii, S.; Armes, S.P. *J. Am. Chem. Soc.* 2009, 131, 5386–5387

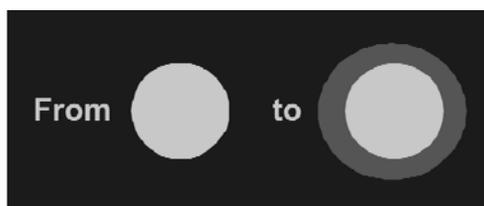
Gold nanoparticles, peptides and cells: the dynamic picture

Raphaël Lévy

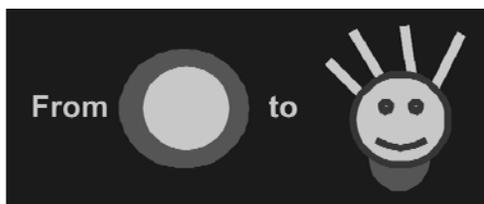
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The self-assembled monolayers (SAMs) of thiolated molecules that form at the surface of gold nanoparticles are dynamic supramolecular systems. The two physical phenomena that allow evolution of these systems are 2D diffusion of ligands in the monolayer and ligand exchange.

These mechanisms provide a way by which the surface can evolve and adapt to external or internal constraints, eventually leading to self-organization, phase separation of the ligands and to the formation of domains in mixed SAMs. This, in turn, opens up the possibility of designing nanoparticles analogous to proteins, i.e. which have a high degree of internal complexity on the molecular scale together with advanced functions.¹ My presentation will be structured in three parts.



In the first part, I will introduce a particular type of SAMs: self-assembled monolayers composed of peptides.^{1, 2} This capping system provides a convenient way to address some of the key constraints that nanoparticles have to meet for applications in biological imaging and biosensing, namely colloidal stability, limited non-specific interactions, and a versatile route to the attachment of functional groups such as targeting or sensing units.



In the second part, I will discuss current efforts towards structured nanoparticles. One of the critical issues for this emerging field is structural characterisation. Using chemical cross-linking, a classical method from the early days of structural biology, we have demonstrated the formation of supramolecular domains in mixed peptide layers.³ Fourier Transform Infra Red (FTIR) spectroscopy of peptide-capped nanoparticles in solution show that some peptides form disordered structures (random coil) while others can be engineered to form ordered supramolecular arrangements (β -sheet).



In the third part, I will discuss the dynamic interaction and evolution of nanoparticle bioconjugates during and after internalization by living cells. We have used a combination of photothermal microscopy and fluorescence unquenching to visualize at the same time the localization of nanoparticles and the fate of the capping layer. Our results have direct implications for the design of all nanoparticle-based intracellular sensors.

Reference:

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- [3] ChemBioChem 2008, 9, 2127

Responsive block copolymer micelles within multilayer films for use as nano-delivery systems

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This presentation will describe our work on the assembly of multilayer films of responsive block copolymer micelles on flat and curved surfaces. Such multilayer films provide a highly functional organized coating that can potentially be used for controlled loading and release of active materials. We will first briefly demonstrate the ability of these systems to retain their integrity when adsorbed at the solid interface. This part of the work involves using quartz crystal microbalance, optical reflectometry and atomic force microscopy techniques to study the structural changes of the adsorbed films. We will then focus on our recent work that illustrates how these structures can be assembled on colloidal sacrificial templates for the preparation of smart microcapsules and how the functionality of the building blocks can provide significant 'tunable' functionality to the walls of the capsules produced. In particular we will discuss how the surface charge density of the micellar building blocks affects the film properties. We will also demonstrate the possibility of further increasing the functionality of such structures by incorporating different types of materials within the constructed shell. Finally, we will also discuss the encapsulation of hydrophobic compounds within the multilayer film and their release from it.

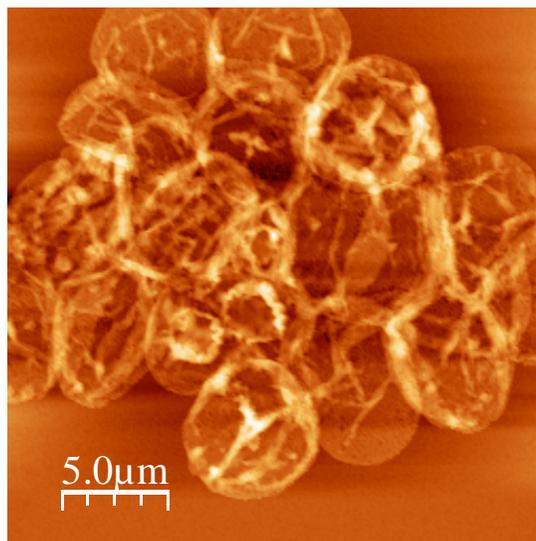


Figure 1. Atomic Force Microscopy image of microcapsules with a shell consisting of a multilayer film of polyelectrolytes and diblock copolymer micelles. The film was initially adsorbed onto calcium carbonate colloidal particles, subsequently dissolved in mild conditions.

Synthesis and assembly of inorganic nanostructures at the oil-water interface

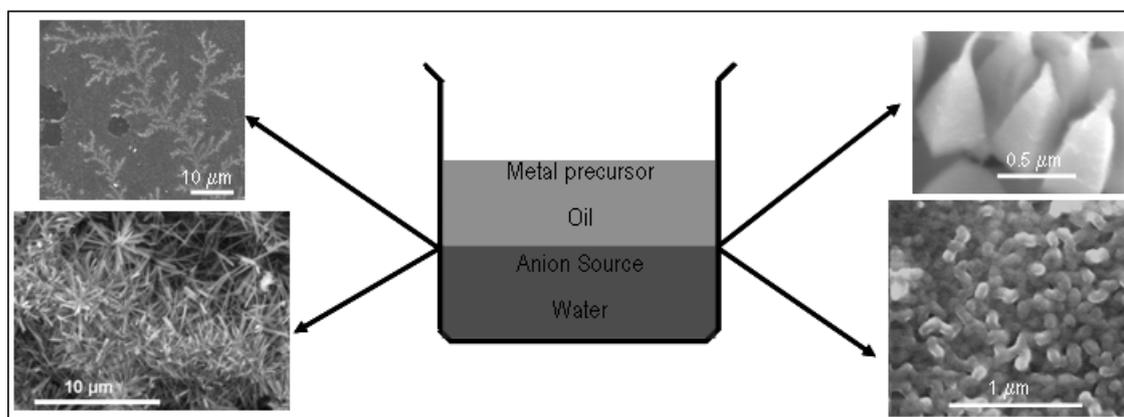
P. John Thomas

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The areas surrounding the interface between two immiscible liquids is of current interest due to their ability to assemble colloidal as well as nanocrystalline particulates. This has seen renewed interest and has been used to generate assemblies of colloidal particles.

This talk will showcase recent results and make the case that the water-oil interface, for long confined to intellectual backwaters, possesses a number of properties particularly suited for the synthesis of nanostructured materials.

In Manchester, we have been successful in using the water-oil interface to synthesize nanorod arrays of $\text{Cd}(\text{OH})_2$ ¹, assemblies of Au nanocrystals², monolayered films of pyramidal PbS crystallites with high energy {113} facets³, nanocrystalline films of CdS, ZnS⁴ and Bi_2S_3 .⁵ The above structures have been obtained by holding a metal precursor dissolved in toluene in contact with an aqueous layer containing a reducing, oxidizing or precipitating reagent. The reaction is mediated by interfacial processes and results in deposits *suspended* in the interfacial region. The interface has a dual role of controlling charge transport and directing the structure of the deposit.



The talk will show that deposition provides a simple, convenient and inexpensive route to high quality films of nanostructures.

Reference:

- [1] S. N. Mlondo, P. J. Thomas, P. O'Brien, *Chem. Commun.*, 2008, 2768-2770.
- [2] S.N.Mlondo, P.J. Thomas, P.O'Brien, manuscript under consideration;
- [3] D. Fan, P. J. Thomas, P. O'Brien, *J. Am. Chem. Soc.* 2008, 130, 10892-10894.
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- [5] D. Fan, P. J. Thomas, P. O'Brien, *Chem. Phys. Lett.* 2008, 465, 110-114.

Gold nanorods for applications in biological imaging*Y. Zhang, D. J. S. Birch and Y. Chen**Department of Physics, Strathclyde University, John Anderson Building
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Nobel metal nanoparticles have great potential for applications in biological imaging and sensing because of their unique optical properties originating from the excitation of local surface plasmon resonances (SPR) [1,2]. In particular, gold nanorods are low toxic, photostable, and have strong and SPR enhanced two-photon luminescence (TPL), suggesting a potential as biological labels in vivo imaging [3]. In this work, gold nanorods were synthesized through a seeded growth process with a length of about 50nm and an average aspect ratio of 3. TPL images from single nanorod were obtained by confocal microscope, and the relationship between the luminescence intensity and the excitation power confirms the two-photon origin. Further more, we investigated the cell uptake and fluorescence of gold nanorods in cells. It is found that nanorods show stable and strong two-photon luminescence with single particle resolution, demonstrating the possibility of using gold nanorods as a fluorescence probe in living cells. Finally, TPL lifetime of gold nanorods were studied using Fluorescence Lifetime Imaging Microscopy (FLIM) to get the dynamical information of two-photon excitation process. Compared with intensity image, the FLIM image provides better resolution and contrast. Moreover, characteristic lifetime of gold nanorods was found in a time scale about 100 ps, in comparison with long lifetime of most fluorescence labelling molecules, such as DAPI (more than 2 ns). Thus, TPL lifetime can be used to identify gold nanorods in a system with multiple labels when emission bands are overlapped, as demonstrated in this work.

Reference:

- [1] R. A. Sperling, P. R. Gil, F. Zhang, M. Zanella and W. J. Parak, *Chem. Soc. Rev.*, 2008, 37, 1896-1908.
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- [3] J. Perez-Jeste, I. Pastoriza-Santos, L. M. Liz-Marzan, P. Mulvaney, *Coordination Chem. Rev.*, 2005, 249, 1870-1901.

Digital Biomagnetism

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Tom J. Hayward, Justin Llandro, Thanos Mitrelias, Adrian Ionescu
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Microarrays and suspension-based assay technologies (SATs) have recently become common-place in biological laboratories for applications from genotyping to 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.

We will present a new form of SAT, which utilizes a novel design of suspended bio-molecular microcarrier containing an addressable magnetic barcode. The magnetic bits are either laterally separated and embedded inside an SU8 backbone or stacked vertically interleaved with non-magnetic decoupling layers. By exploiting various combinations of shape anisotropy, composition modulation and controlling the magnetic grain microstructure we are able to engineer different coercivities for each bit. This methodology allows an arbitrary code to be written to these structures using a non-local magnetic field. Shape anisotropy is used to constrain the magnetisation direction into one of two stable directions, corresponding to a binary barcode. The binary nature of these tags means that for every additional magnetic bit added to the structure, the number of possible codes doubles, hence an exponentially increasing tagging system. Another advantage of magnetic tagging over conventional microcarriers is that the tags fabricated are nominally identical before being written giving massive economy of scale.

The SU8 based planar tags, where the epitaxial cobalt elements are encapsulated inside a polymer shell, are created using a multi step lithography process. They offer a short term solution, giving up to a possible 8192 codes, more than ample for many biological and chemical assays. The pillar architecture is aimed at a longer term goal of offering up to 4 billion different codes, suiting genotyping and sequencing. These are grown by electrodeposition from a single electrolytic bath containing both the magnetic and non magnetic metallic ions. The advantage of this technique is that multilayer structures can be easily grown and automated without repeated transfer cycles. The biofunctionalisation of these tags is achieved through a gold capping layer, also grown by electrodeposition, which facilitates self assembled monolayer growth as the first step of chemical functionalisation.

We demonstrate that both 5-bit planar tags and 2-bit pillar tags with individually switchable bits have been created and characterised. Microfluidic flow and control of the planar tags over magnetoresistive sensors, which are capable of detecting individual magnetic elements, is also presented.

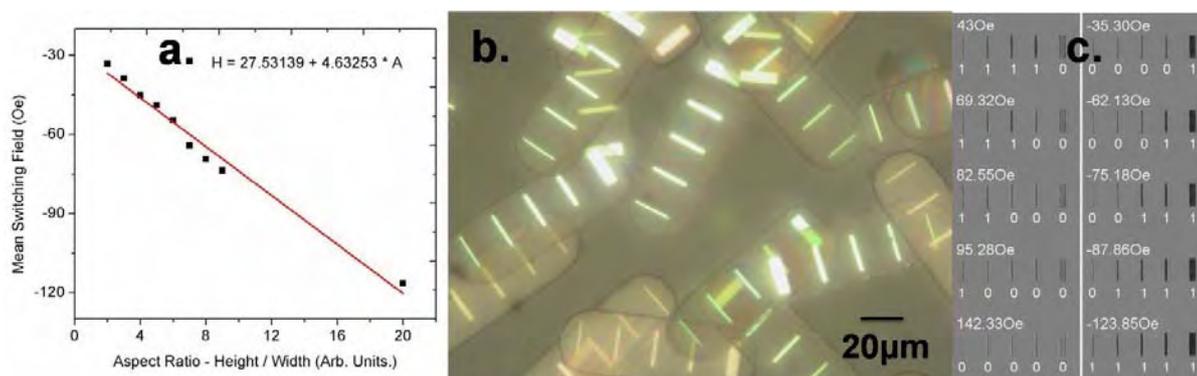


Figure 1. For the planar tags (a) Aspect ratio of magnetic elements versus the mean switching field, (b) Free floating 5-bit planar tags in water and (c) Magnetic domain images to demonstrate writing and optical detection.