Supported, cluster-derived multimetallic nanoparticles for the generation of a second generation hybrid biofuel

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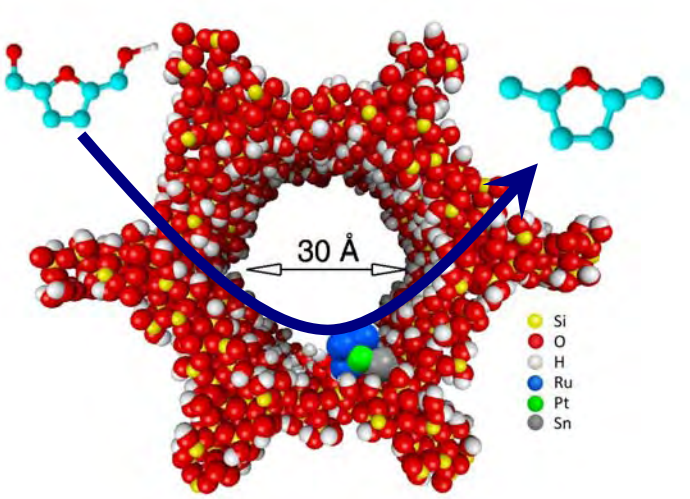

There has been much discussion and research in to suitable alternatives to ethanol produced by fermentation, for use as an automotive fuel and gasoline replacement. One focus has been furanic compounds, which are produced by the acid-catalysed dehydration of hexoses[1, 2]. The focus of our work is 2, 5-dimethylfuran (DMF) production by hydrogenation of 5-hydroxymethylfurfural (HMF)[2]. The current state of the art is a gas phase reaction in continuous flow. Our catalysts are mixed-metal nanoparticles supported on mesoporous silica, formed from molecular clusters on the silica surface, by gentle thermolysis under vacuum[3].

Previous work has shown that inclusion of tin in the precursor compounds leads to catalysts with improved selectivity towards less-hydrogenated species in multiple hydrogenation reactions[4]. We have shown that ruthenium-platinum-tin nanoparticles derived from the cluster give good selectivity for DMF in the liquid-phase hydrogenation of HMF.

Nanoparticles were generated from the precursors $Ru(CO)_4(SnPh_3)_2$, $Pt(COD)(SnPh_3)_2$ (COD = 1,5-cyclooctadiene), $PtRu_5(CO)_{15}(\ -SnPh_2)(\ _6\text{-C})$ and $Pt_2Ru_2(SnBu^t_3)_2(CO)_9(\mu\text{-H})_2$. The precursor compounds were mounted on mesoporous silica (Davisil 923) by stirring a hexane: dichloromethane solution overnight. Loading was sufficient to give 3wt% metal on silica. The catalyst was activated by heating the powder under vacuum for two hours.

In batch reactions at 150°C and 20 bar H_2 using DMSO as solvent, the trimetallic catalysts gave higher conversions of HMF, with high selectivity to DMF, after 3 hours than did the bimetallics, indicating a synergistic effect between the different metals.

In situ IR spectroscopic data of CO adsorption has indicated that tin acts to improve site isolation of the catalytically active metal centres. This data will be presented at the conference.

We wish to thank UOP LLC of Des Plaines, Iowa, EPSRC and the British-Italian Partnership for funding this work.

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[3] D. S. Shephard, T. Maschmeyer, B. F. G. Johnson, J. M. Thomas, G. Sankar, D. Ozkaya, W. Z. Zhou, R. D. Oldroyd, R. G. Bell, *Angewandte Chemie-International Edition in English* 1997, *36*, 2242.
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Design and production of stimuli-responsive microcapsules

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Over the last decade, there has been a large interest in designing encapsulating structures that can control the delivery of actives in response to changes in their environment. For this purpose, it is worth exploiting the properties of stimuli-responsive polymers within the shell of the designed capsules. Here, we present our work related to the preparation of core-shell nanoparticles, where the solid core is coated with a responsive polymer. These particles are subsequently used for the stabilisation of oil-in-water emulsions as part of a procedure to use solid-stabilised emulsions as templates for the preparation of responsive microcapsules.

We present our different methods for the preparation of a range of responsive core-shell nanoparticles to be used for this purpose. Polystyrene and gold nanoparticles have been coated with the homopolymer poly[2-(dimethylamino)ethyl methacrylate (PDMAEMA) and copolymers derived from it. The particles were prepared using emulsion polymerisation in the case of latex particles as well as grafting of the polymer to the surface of suitable solid particles in the case of gold nanoparticles. In the latter procedure, we improve on the previous method reported in this area by using the responsive properties of the polymer to facilitate rapid adsorption of the polymer to the particle surface. This consequently leads to a faster grafting procedure and higher polymer densities. The PDMAEMA polymer is both pH and temperature responsive and we demonstrate a responsive behaviour of the core-shell particles in suspension with respect to the same stimuli.

Additionally, we present our recent work to use these particles as emulsifiers for the production of monodisperse oil-water emulsions in large-scale. Responsive polystyrene particles will be used in this case to demonstrate the possibility to produce such emulsions from a membrane emulsification apparatus. In this process the oil phase is pushed through a membrane into the continuous phase containing a dispersion of the particles. As the droplets grow from the pores the particles adsorb to the oil-water interface precipitating the responsive polymer and providing colloidal stability to the emulsion. This method produces stable emulsion droplets in the range of few hundred microns (Figure 1). We show a systematic study of this process demonstrating that not only pH and salt concentration but also the mechanical parameters of emulsification have a large effect on the stability of the emulsion droplets.

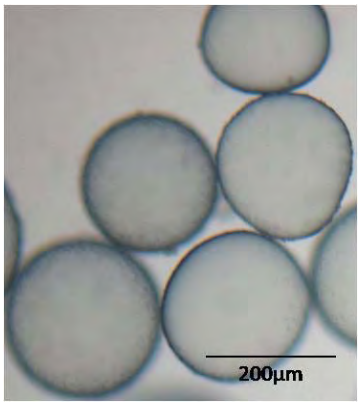

Figure 1. o/w emulsion droplets stabilised by responsive colloidal particles

Intracellular delivery and fate of peptide-capped gold nanoparticles

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Gold nanoparticles have extraordinary optical properties that make them very attractive single molecule labels. Although understanding their dynamic interactions with biomolecules, living cells and organisms is a prerequisite for their use as *in situ* sensors or actuators. While recent research has provided indications on the effect of size, shape, and surface properties of nanoparticles on their internalization by living cells, the biochemical fate of the nanoparticles after internalization has been essentially unknown.

Here we show that peptide-capped gold nanoparticles [1-4] enter mammalian cells by endocytosis. We demonstrate that the peptide layer is subsequently degraded within the endosomal compartments through peptide cleavage by the ubiquitous endosomal protease cathepsin L. Preservation of the peptide layer integrity and cytosolic delivery of nanoparticles can be achieved by a combination of cathepsin inhibition and endosome disruption. This is demonstrated using a combination of distance-dependant fluorescence unquenching and photothermal heterodyne imaging [5-7]. These results prove the potential of peptide-capped gold nanoparticles as cellular biosensors.

Current efforts focus on in-vivo labeling of the nanoparticles and the development of photothermal microscopy for single nanoparticle imaging in living mammalian cells.

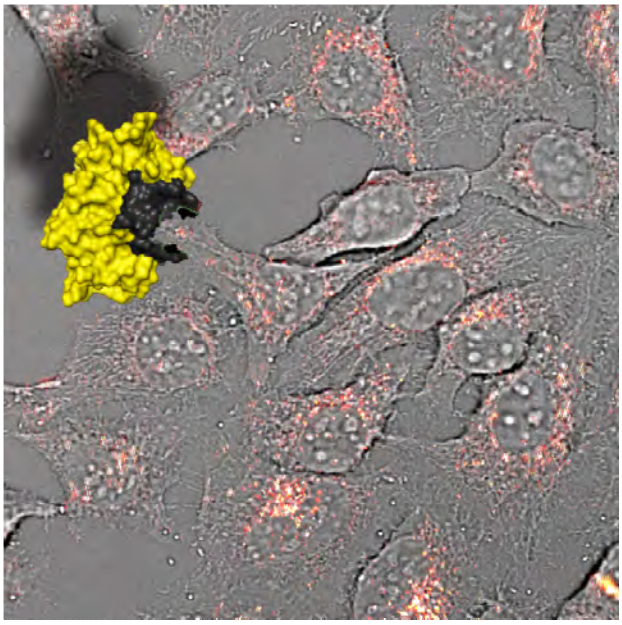

Figure 1. Intracellular degradation of peptide-capped gold nanoparticles by the endosomal protease cathepsin L.

Reference:
[1] R. Lévy et al., J. Am. Chem. Soc. 126, 10076 (2004).
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[7] Berciaud et al., Nano Letters 5, 515 (2005).

Protease modification of peptide-capped and pegylated nanoparticles: interfacial enzyme dynamics and live cell imaging of nanoparticle fate

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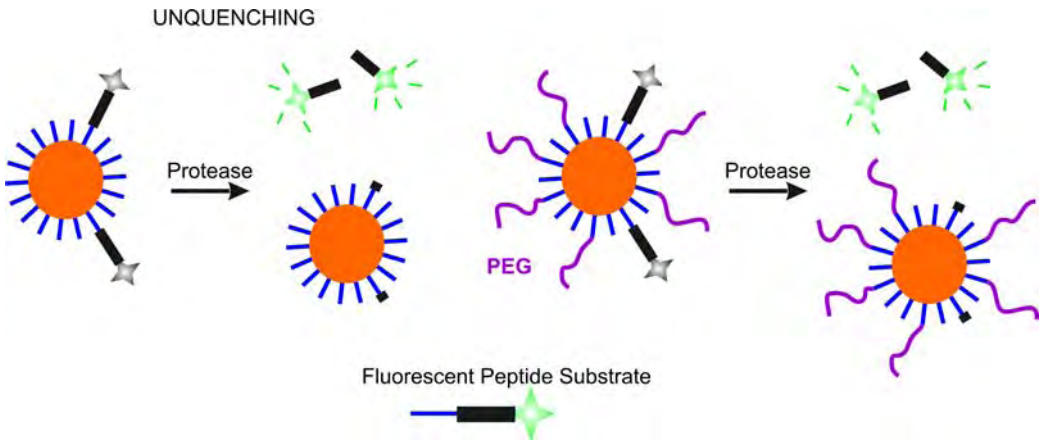
Gold nanoparticles (GNPs) have extraordinary optical properties that make them very attractive single molecule microscopy labels. Several critical issues need however to be solved in order to unravel their full potential for applications inside living cells. In particular, non-specific binding, chemical stability of the probe within the cell (ligand exchange, proteolysis), intracellular delivery of the NPs, and specific attachment to the ligand are all significant challenges.

Peptide-capped gold nanoparticles are easily obtained through the formation of mixed self-assembled monolayers (SAMs). These nanoparticles are stable in a wide range of pH and ionic strengths[1]. Multiple functional groups can be incorporated in a controlled manner in the SAMs[2,3].

Here we use distance-dependant fluorescence quenching to measure the activity of proteases on peptide-capped gold nanoparticles.

We report quantitative measurement of the activity of thrombin on a substrate attached to a gold nanoparticles and on the effect of the surrounding environment. We show that when the peptide substrate is part of a PEGylated SAM, the interfacial kinetics of proteolytic degradation is significantly lowered.[4]



In living cells, we show that degradation of the peptide layer occurs upon internalization of fluorophore-modified peptide-capped GNPs. This degradation takes place in endosomal vesicles and we demonstrate that the enzyme responsible for this degradation is Cathepsin L.[5]

Reference:
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[2] Wang, Z.; Lévy, R.; Fernig, D. G.; Brust, M.; *Bioconj. Chem.* 2005, *16*, 497-500.
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[4] Free, P.; Shaw, C. P.; Lévy, R.; *Chem. Comm.*, 2009, DOI: 10.1039/b910657j
[5] Sée, V.; Free, P.; Cesbron, Y.; Nativo, P.; Shaheen, U.; Rigden, D.; Spiller, D.; Fernig, D.; White, M.; Prior, I., Brust, M.; Lounis, B.; Lévy, R.; *ACS Nano*. 2009, submitted

Deceiving cells by StreptolysinO assisted delivery of gold nanoparticles

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Understanding and controlling the cellular uptake and fate of bioconjugated gold nanoparticles has direct implications for their research and clinical applications. The general picture is that most cell lines internalize most nanoparticles through endocytosis resulting in nanoparticles trapped in endosomes. This severely restricts the potential applications and also results in the degradation of the nanoparticle capping layer through proteolysis. Avoiding endosomal trapping is therefore a key focus of research.

Here we present an original attempt using StreptolysinO (SLO), a 61 kDa secreted bacterial protein (toxin) which is a pore-forming agent that has been used previously as a simple and rapid means of introducing oligonucliotide[1] and siRNA in live cells.[2]

SLO makes the plasma membrane reversibly permeabilized. SLO monomers in solution first bind reversibly to the membrane. Two membrane-bound monomers then react to form a membrane-inserted dimer, which by rapid association of further monomers is extended into arc-shaped and finally, along with oligomer growth, ring shaped complexes constituting transmembrane pores are formed.

Our initial results confirm that more gold nano particles are uptaken in cells which have been treated with SLO than in untreated cells (Fig: 1). We are also studying the effect of partial nanoparticle coverage with PEG (poly ethylene-glycol) on SLO assisted delivery of gold nanoparticles. PEG is normally used to avoid non specific interaction with cells and it also results in a very significant diminution of passive uptake by living cells.

We are currently combining fluorescence microscopy, photothermal microscopy and electron microscopy to elucidate the mechanisms, localization and fate of the nanoparticles uptaken during the SLO treatment.

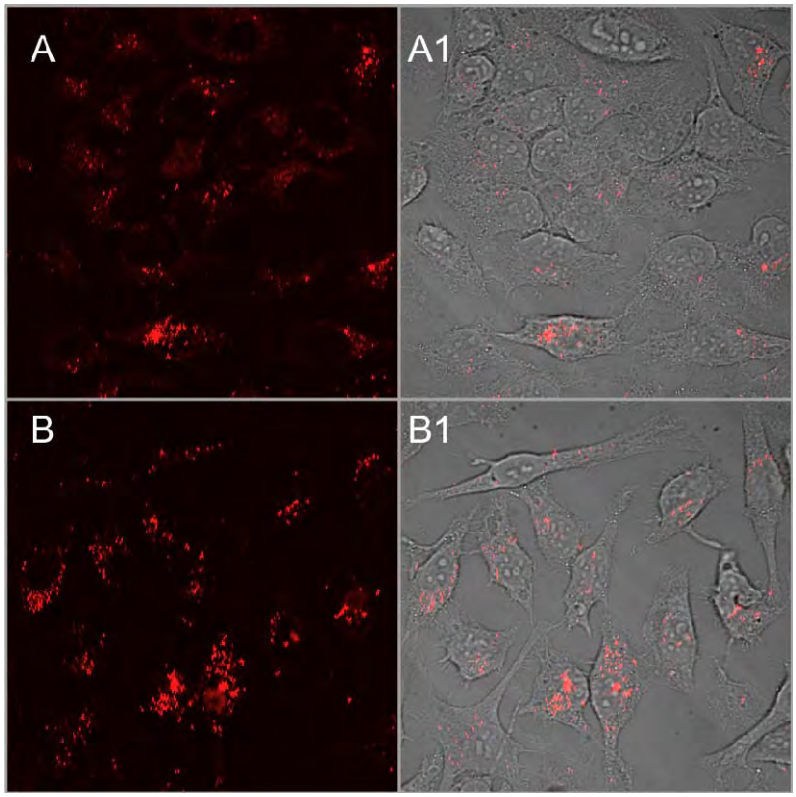

Fig:1

HeLa cells incubated with 5% CCALNN-PEG - 95% CALNN coated 5 nm Au NPs(60nM,final conc.) for10 minutes with and without SLO, A) photothermal image without SLO, A1) overlay of the photothermal and bright field images without SLO, B) photothermal image with SLO, B1) overlay of the photothermal and bright field images with SLO

Reference:
[1] "Nuclear delivery of antisense oligodeoxynucleotides through reversible permeabilization of human leukemia cells with streptolysinO", Spiller DG, Tidd DM, Antisense Res Dev. 1995 Spring; 5(1):13-21.
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Engineering peptide self-assembled monolayers on gold nanoparticles

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Since the development of stable nanoparticles approximately 50 years ago, they have been the subject of much interest with applications in fields as diverse as catalysis, therapeutics, electronics and diagnostics.

In 2004 peptides were shown to increase the colloidal stability of gold nanoparticles by forming a self assembled monolayer (SAM) (1). This SAM imparts both high physical and chemical stability, which is essential for applications in biological systems. Because of the variety of the chemical properties of amino acids, it also opens the route to the engineering of complex protein-like. One particular challenge is to control the formation of domains and secondary structures with the long term goal of being able to engineer self-assembling, self-organising capped nanoparticles. We will report on recent experimental evidence indicating the formation of domains in mixed monolayers of peptides and on structural studies, using Fourier Transform Infra-red Spectrometry (FTIR), demonstrating the formation of supramolecular structures (β -sheet) at the surface of nanoparticles.

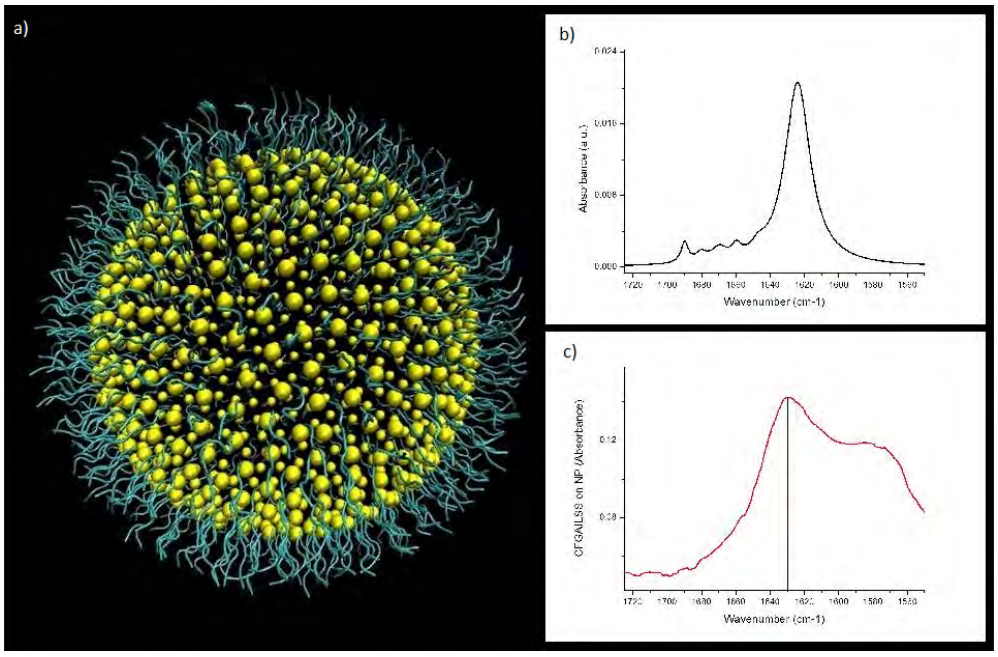

Figure 1. Structures on peptide-capped gold nanoparticles Molecular Dynamics simulation (a) and FTIR (b) of a CALNN self-assembled peptide monolayer, consistant with a random coil structure. b) and c) FTIR demonstrates the presence of peptide secondary structure in peptide monolayers (top and bottom right)

Reference:
[1] Lévy, R., Thanh, N. T. K., Doty, R. C., Hussain, I., Nichols, R. J., Schiffrin, D. J., Brust, M., Fernig, D. G. (2004) Rational and Combinatorial Design of Peptide Capping Ligands for Gold Nanoparticles, *J. Am.Chem. Soc*. 126, 10076 – 10084

Al_2O_3 and Ta_2O_5 nanoparticle production by arc-discharge in water for flexible dielectrics

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Lately, nanoparticle production has attracted the interest of numerous research groups around the world due to the variety of biological [1] and electronic [2] applications. Here, the process of fabricating dielectric nanoparticles (NPs) using the arc-discharge in water method and their inclusion in organic layers are presented.

This cost efficient method uses a current source of 35 A to create an electric arc between two rod electrodes (6.35 mm in diameter) immersed in de-ionized water. The cathode rod is always carbon whereas the anode is a pure metal; in our case Aluminium or Tantalum.

Electrical and optical characterization of the system has been carried out by recording the voltage, current and emitted light intensity simultaneously during the arc-discharge. In addition, Optical Emission Spectroscopy (OES) has been used to monitor the evolution of the plasma species and the production mechanism is briefly discussed. The nanoparticles were studied using High Resolution Electron Microscopy (HREM), X-Ray Diffraction (XRD) and X-ray Photoelectron Spectroscopy (XPS). Figure 1 shows clusters of a) Al_2O_3 and b) Ta_2O_5 NPs.

The dielectric properties of the NPs were determined from the capacitance of composites prepared by embedding the produced NPs in a dielectric polymer matrix. The addition of the produced NPs showed significant enhancement of the dielectric constant of the composite. The leakage current in the pure and composite matrix was measured in the same order of magnitude, further confirming that the produced material is predominantly made of dielectric NPs (Figure 1c depicts a cross-section of a polymer-NP composite).

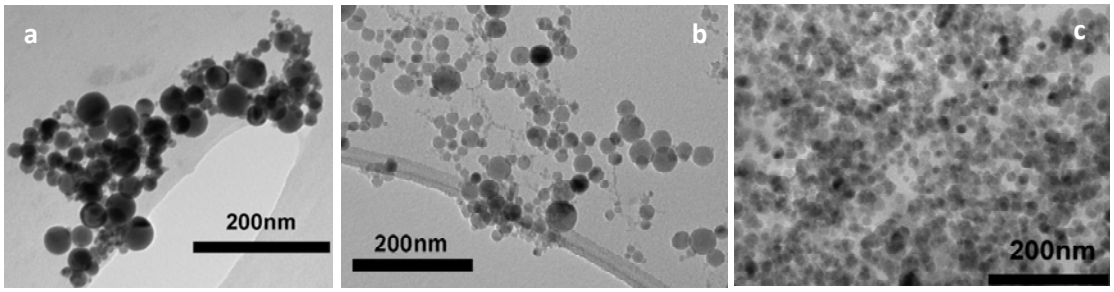

Figure 1: TEM micrographs showing a) Al_2O_3 and b) Ta_2O_5 clusters, and c) embedded NPs in dielectric polymer matrix.

Reference:
[1] " Nanopartcles for bioimaging", P. Sharma, S. Brown, G. Walter, S. Santra, B. Moudgil, Adv. Colloid Interface Sci. 123, 2006, 471-485.
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Gold-copper alloy nanoparticles as potential catalyst for CO_2 electroreduction

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Alloys have attracted considerable attention in material science owing to their properties that can be superior to those of the constituent metals. In addition multifunctionality induced in the alloys, depending on the number of phases, can help in their use as catalytic materials for different reactions. Copper is a well-known electrocatalyst for the reduction of carbon dioxide resulting in a variety of products[1] involving the formation of C_1 to C_5 organic compounds. Its enhanced sensitivity towards air oxidation, however, makes Cu less stable regarding its catalytic efficiency. A corrosion-resistant metal can be alloyed with copper to produce more stable materials[2]. Gold-copper bimetallic nanostructures have been synthesized and these have been found to be highly stable towards oxidation. These alloy nanoparticles can be employed as bifunctional catalyst for the reduction of CO_2. An unusual property of these materials is the appearance of a miscibility gap in the particles of size in the nanometre range. An image of these core-shell particles is shown in Figure 1. This work will discuss the formation and properties of these core-shell materials.

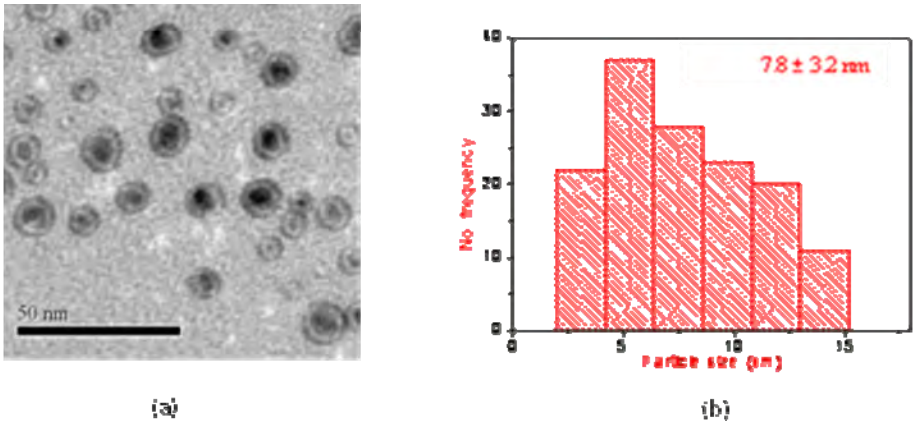

Figure 1. TEM image (a) of the gold-copper core shell nanoparticles and the histogram for particle size distribution (b).

Reference:
[1] “A review of the aqueous electrochemical reduction of CO2 to hydrocarbons at copper”, M. Gattrell, N. Gupta, A. CO, *J. Electroanal. Chem.* 594[1], 2006, 1-19.
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Nanoparticles in criminal detection (NICD)

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Despite all the advances in the use of DNA for crime detection, fingerprints remain one of the most useful forms of evidence in identification and proof of identity. Any technique for enhancing latent fingerprints must give a contrast between the fingerprint itself and the background of the substrate. Fingerprints mainly consist of water, but there are many other components to them. These include amines and carboxylic acids from proteins and amino acids.[1] Current chemical techniques used to detect latent fingerprints on non-porous substrates involve superglue evaporation followed by staining with fluorescent dyes. Porous surfaces are generally treated with a solution of ninhydrin which leaves a purple coloured compound.

However, there are many occasions when fingerprints cannot be visualised using these techniques because they are on unsuitable substrates or are too faint. One promising approach to the enhancement of fingerprints is to use luminescent semiconductor nanoparticles as the detecting agent.[2-5] Contrast between fingerprint and background can be obtained by wavelength and/or time resolved fluorescence measurements. We have been designing target ligands for surface modification of fluorescent nanoparticles. This enables chemical binding to fingerprint residues (Figure 1). [6]

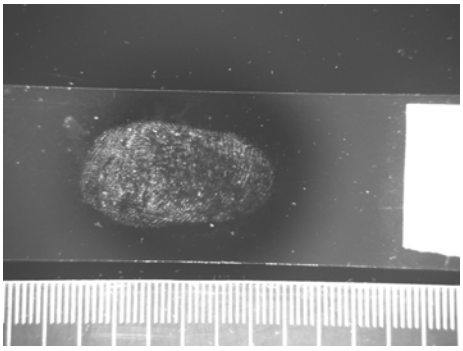

Figure 1. Photograph showing enhanced fingerprint on glass using our modified nanoparticle solution.

Reference:
[1] “Recent advances in photoluminescence detection of fingerprints”, E. R. Menzel, The Scientific World, 2008,1, 498-501
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J.R. Amey, D.J. Cole-Hamilton, I.D.W. Samuel, J. Bond. Patent Application (filed 18th June 2008): GB 0811170.0

Interaction of nanoparticles and radiation

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Electromagnetic radiation and matter interact predominantly by three different mechanisms: Compton scattering, the photoelectric effect and pair production. With the photoelectric effect, electrons absorb the incident photon energy and are either emitted or lose energy in secondary processes. For energies below 1 MeV, the photoelectric effect is the predominant one. The cross section for the photoelectric effect is proportional to Z (atomic number) to the power of five and roughly proportional to the incident photon energy to the power of -7/2.

Most of the photoelectrons produced in an absorbing material lose their energy through electron-electron scattering and Bremsstrahlung. Typically the escape depth of photoelectrons generated within solids is between 0.5 and 5 nm [1]. Hence, irradiated particles with diameters in the range of a few nanometers will emit most of the generated photoelectrons without re-absorbing. Therefore, nanoparticles are likely to emit the largest quantity of secondary electrons proportional to their mass.

Secondary electron emission of high Z materials could help to understand the toxicity of various heavy metals. This may be crucial in explaining the toxicity of nanomaterials with a high atomic number Z [2].

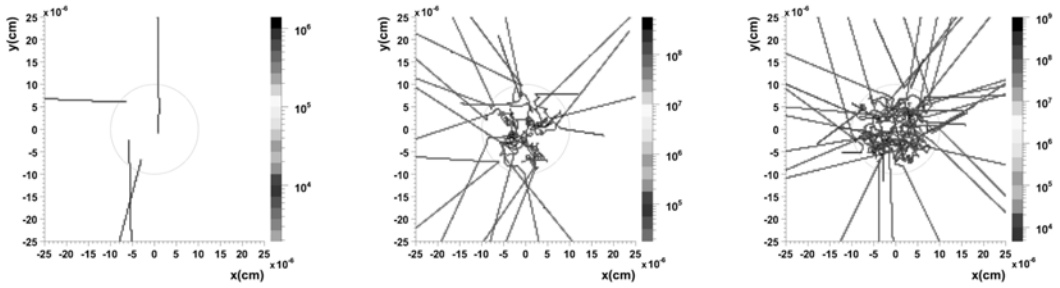

Figure 1. Secondary electron production of a 10nm water, gold and uranium particle (from left to right) by 10 keV primary photons (shown for 100.000 primary photons in the case of water, 1.000 in the case of gold and uranium).

We employed Monte-Carlo-Simulations to model the number and energy of secondary electrons released by nanoparticles of different sizes and chemical compositions. The Monte-Carlo Code used is derived from the FLUKA-project [3], a Monte-Carlo-Toolkit developed by INFN and CERN to model various matter-radiation interaction mechanisms. We report quantitative findings for a number of elements and experimental data on gold nanoparticles.

Reference:
[1] S Huefner, Photoelectron Spectroscopy: principles and applications, Springer, Berlin 1996
[2] Busby C (2005), Does Uranium contamination amplify natural background radiation dose to the D.A? *Eur. J. Biol. Biolmagn*. 1 (2), 120-131, 2005
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CERN-2005-10 (2005), INFN/TC_05/11, SLAC-R-773

Synthesis of nnoparticles in agarose gel

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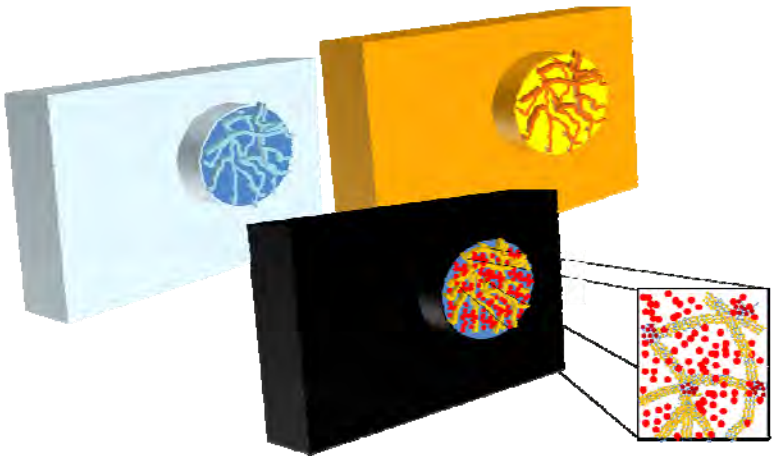
In past decades, research efforts were concentrated on the synthesis of metal particles especially the preparation of gold colloids. A large number of synthetic methods are known and have been reviewed extensively[1]. In most cases, these rely on wet chemical processes which are most suitable for obtaining narrow size distributions and the desired shape. The synthesis of the same metallic particles in complex fluids such as gels or extremely viscous media adds several other parameters to be taken in consideration, notably the diffusion of the chemical compounds through the matrix fluid.

Based on this approach, studies have been carried out on the use of hydrogel networks as three dimensional molecular templates for the formation of metallic nanostructures. UV-visible spectroscopy, X-ray diffraction, and different methods of Electron Microscopy (TEM, STEM and HAADF-STEM) were used to characterise the samples produced.

Interestingly, we have found that gels are excellent matrices for the formation of nanoparticles from 0.5 to 4nm, which tend to decorate the internal molecular network structure of the gel. This synthesis works for Au, Pd, Pt, Ru and Ag nanoparticles.

The effect of metal loading on the electrical transport properties of the gel has been studied. Owing to their tuneable charge transport properties the materials prepared show promise for the development of sensors. Finally, the use of Ag loaded agarose gel as substrate for ultra-sensitive detection of molecules via SERS has been studied. Because the gel can collapse upon drying and recover when rehydrated, it can be foreseen as an excellent mechanical molecular trap. Additionally it gives rise to dynamic hot spots as the network volume decreases and the silver particles get close to each other, thereby generating the huge electromagnetic fields that are needed for ultra-detection.



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Synthesis and properties of water-soluble ferrocene-modified gold nanoparticles

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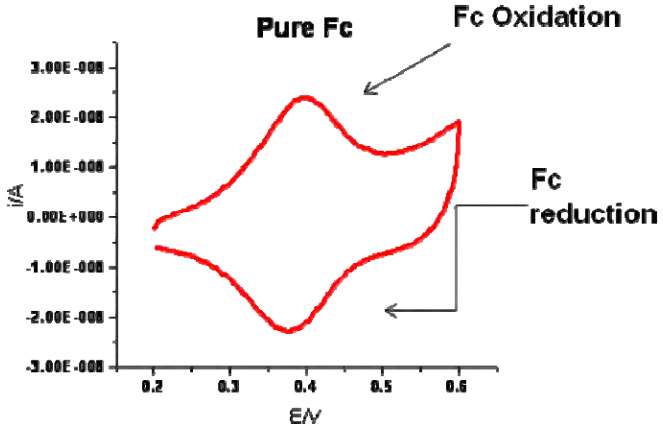
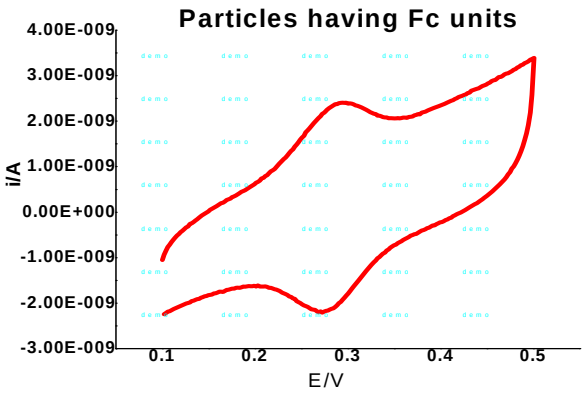
Gold Nanoparticles have been extensively used as a model system for drug delivery as they are known to be least toxic for the living systems and can be efficiently used as drug carriers. Here we demonstrate the modification of mercaptoalkyl-oligoethyleneglycol-stabilised gold nanoparticles (PEG-GNPs) with well-known anti-cancer drug *i.e*. ferrocene derivatives. Ferrocene has been discussed as a potential anti-cancer agent that is active by causing oxidational damage to DNA. Unfortunately, it is practically insoluble in water, which makes its delivery to the site of activity very difficult within a biological environment. The thiol-modified ferrocene is readily solubilised when attached to highly water-soluble PEGylated gold nanoparticles. Importantly, it retains its redox activity under these conditions as shown by electrochemical studies. The presence of the iron in the molecule provides a convenient handle to quantify the amount of ferrocene in the ligand shell, which here has been done by atomic emission spectroscopy and electrochemically. It is shown that the loading of the particles with ferrocene can be controlled quite well without compromising solubility until the ligand shell contains a proportion of about 10 mol.% ferrocene. Cell viability studies and preliminary attempts of nuclear targeting are also reported.





Figures 1 and 2. Electrochemical Characterization. Fc=Ferrocene Derivative

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