Project no. NMP4-CT-2005-014006

Project acronym: NANO3D

Project title: Precision Chemical Nanoengineering: Integrating Top-Down and Bottom-Up Methodologies for the Fabrication of 3-D Adaptive Nanostructured Architectures

Instrument: Specific Targeted Research Project

Thematic Priority Three

EXECUTIVE SUMMARY OF WORK CARRIED OUT IN YEAR 1

Period covered: from 1/6/2005 to 31/5/2006 Date of preparation:9/2006

Start date of project: 1/6/2005 Duration: 36 months

Project coordinator name: Professor Jon A Preece
Project coordinator organisation name: The University of Birmingham
Revision [final September 2006…]

EXECUTIVE SUMMARY OF WORK CARRIED OUT

Summary Description of Project Objectives

The overall objective of the research is to integrate top-down lithographic techniques which enable precise spatial patterning of surfaces from micron- to the nanoscale, with the controlled stepwise self-assembly and self-organisation of nanometer scale (bio)chemical entities to these surfaces, to fabricate three dimensional (3D) adaptive nanostructured architectures, which have demonstratable uses, in a fashion that will allow the processes to be scaled into proto-type production methodologies.

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3	Max Planck Institute for Polymer Chemistry	Ulrich Jonas	MPI	http://www.mpip-mainz.mpg.de	Germany
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Work and Results Performed To Date

Overview of Progress and Interactions Between the Nano3D Consortia

Year 1 of the Nano3D project has seen good progress in all areas of the project plan, with extensive interaction between partners either in terms of joint meetings, laboratory visits or exchange of materials. The consortia have met three times during the first year to assess progress and establish project plans for the proceeding months, and there have been specific interactions between (i) BAE, TYN, 9D and UB with respect to the design of the platform wafer, (ii) TYN and UB with respect to supply and fabrication of materials for nanowire production, (iii) UB and 9D with respect to supply of suspension of colloidal nanoparticles for use in the inkjet printing process, (iv) 9D, TYN and BAE with regards to the design of the microfluidics system on to the platform wafer, (v) UB, MPI and BAE with respect to using a thermal AFM probe for writing to surfaces, and (vi) CSIC and TYN with respect to the use of peptides to direct assembly of particles.

Highlighted in **Figure 1** is a schematic overview of the project. During year 1 the consortia have designed and synthesised materials that will allow self-assembled monolayer formation on surfaces (Stage 1), that can also be written to and/or printed to (Stage 2), as well as subsequently have nanomaterials assembled to the patterns (Stage 3). Furthermore, materials have been designed and synthesised (polyelectrolytes and nanomaterials) that will allow multiple self-assembly steps (that will contribute to Stages 4 and 5). Finally, the consortia has been able to fabricate surfaces that are adaptable to the environment (e.g. swelling and contracting).

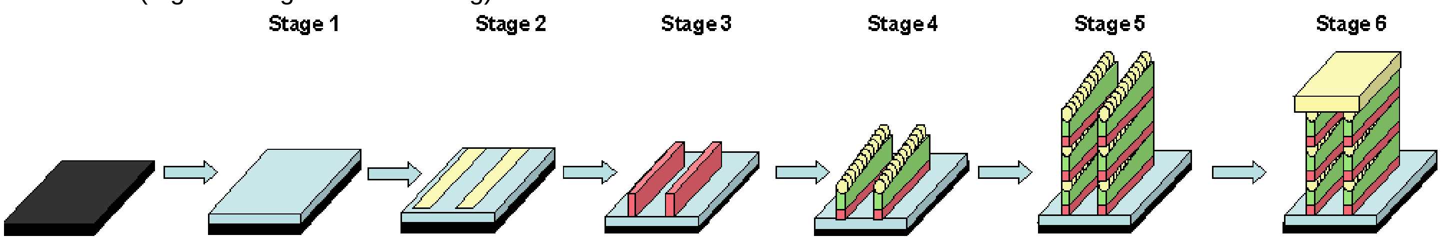

Figure 1. Overview schematic of the Nano3D project

The following sections detail the scientific highlights of the research carried out to date.

Highlights of Research During Year 1

Platform Wafer Design

The platform wafer design (Figure 2) is crucial to the project as several writing methodologies (e-beam, SNOM, AFM) have to be accessible to the surface of the wafer, on multiple occasions. Therefore, the wafer design has to be of the appropriate dimensions to be compatible with the various techniques, but also be addressable in a fashion that it is straightforward to re-find areas that were written to previously. Thus, the design required input from several of the consortia members who had access to the various writing methodologies.

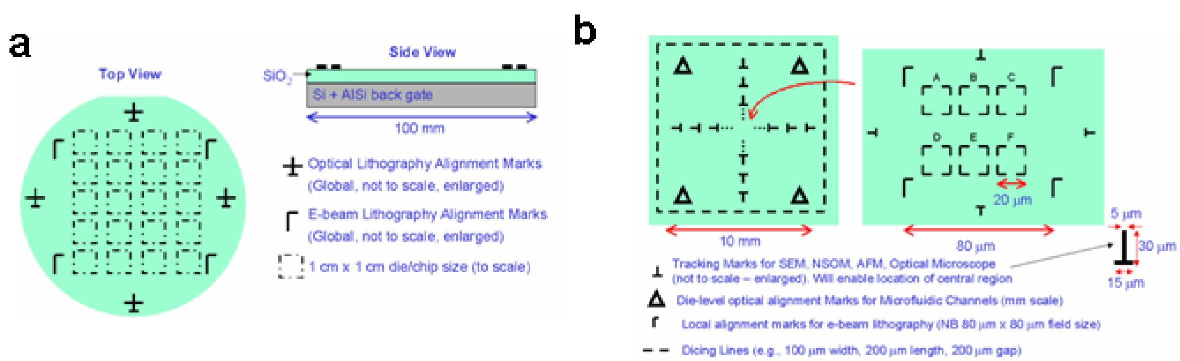

Figure 2. **a)** Schematic of preliminary design for wafer-scale layout, including alignment marks for optical and e-beam lithography, and also dice borders for individual dies. **b)** Die-level layout, tracking marks to locate central fields, local alignment marks for e-beam lithography, and also die-level alignment marks for microfluidic channels.

Synthesis of Silanes to Form Self-Assembled Monlayer (SAMs) on the Platform Wafer

The SiO_2 platform wafer surface requires self-assembled monolayers of silanes to be formed (Stage 1) that can subsequently be patterned with light, electrons, x-rays, or heat (thermal AFM) (Stage 2). To this end UB and MPI have synthesised such materials. A light sensitive silane is shown in Figure 3, which contains a latent amino group that will be revealed upon light irradiation. In addition, MPI have materials that will reveal acid moieties upon heat exposure. UB have materials that will reveal an amino group upon e-beam and x-ray exposure, and gold upon light exposure.

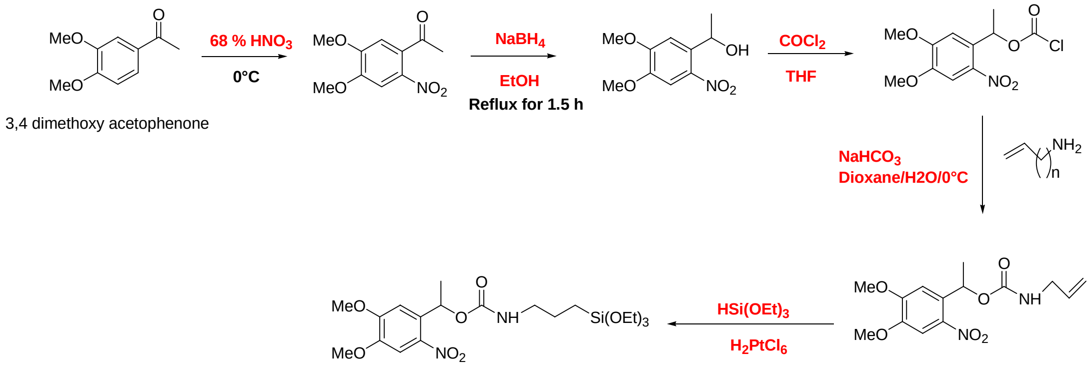

Figure 3. Synthesis of amino light-protected amino-silane.

Fabrication of Non-Adaptive 3D-Nanostructures

A core objective of this project is to not just nanopattern surfaces, but to also building into the third dimension to afford 3D-nanostructured surfaces. To this end a novel one step route to both nanopatterning and building in to the third dimension has been devised. This process relies upon fabricating a surface covered with alkylthiol passivated gold nanoparticles and then utilising the photochemical induced thiolate to sulfonate oxidation. The resulting sulfonate is bound relative weakly to the gold nanoparticle and depassivates from the gold, resulting in the gold cores fusing together. Thus, using a scanning near field optical microscope (SNOM) as a photon-writing tool (Figure 4a) 60 nm wide gold wires can be written on to the SiO_2 surface (Figure 4b) (a combination of Stages 2 and 3).

In addition, by a combination of micro-contacting printing of dodecanethiol to a 100 nm thick film of gold on SiO_2 (Stage 2), and etching (using the thiol as a negative tone resist), it proved possible to make 22 nm high pillars of gold (Figure 4c) (Stage 3).

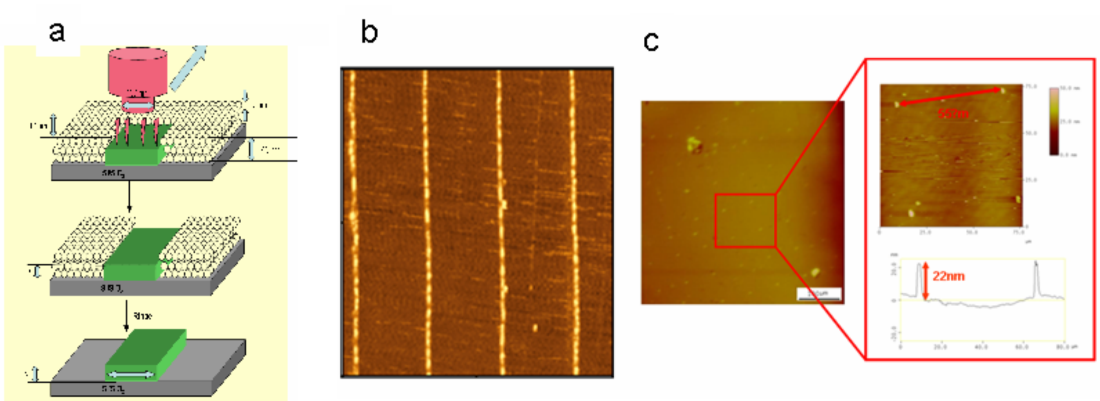

Figure 4. **a**) Schematic representation of witing to gold nanoparticles with the SNOM, **b**) gold nanowires formed after writing to an SiO_2 surface coated alkylthiol passivated particles with a SNOM, and **c**) Nanoscale structures created via a combination of micro-contact printing and chemical etching.

Non-Adaptive Polyelectrolytes

Synthetic methodologies to rigid organic polyions (Figure 5) are being developed as key components in the so-called layer-by-layer deposition (LBL) on surfaces. The requirement for these molecular materials to be rigid is to enable structurally well-defined growth on the patterned surfaces to afford high aspect ratios, when sequentially adsorbed with a nanoparticles (Stages 5 and 6).

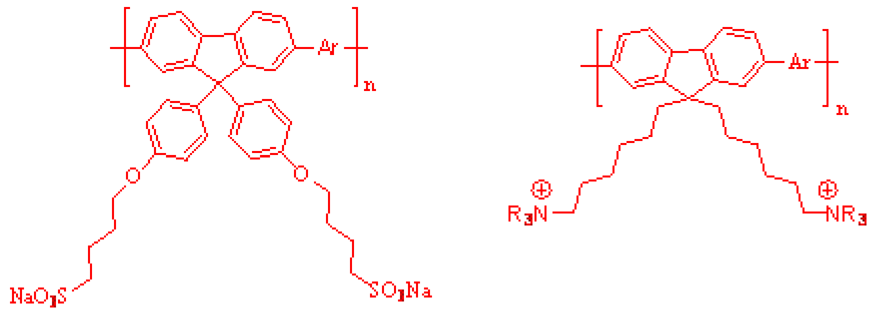

Figure 5. Target rigid organic polyions for LBL deposition.

Adaptive Polyelectrolytes

A unique part of the Nano3D consortia's approach is the introduction of adaptive materials in to the walls (Stages 4 and 5), that will allow them to respond to the environment, which will allow potential applications in sensors and delivery vehicles (drugs, for example). Thus, Figure 6 highlights the synthesis of a hydrogel (Figure 6a), that can swell and deswell repeatedly (Figure 6b), as well as be further chemically modified in order that it may respond to changes in pH or temperature.

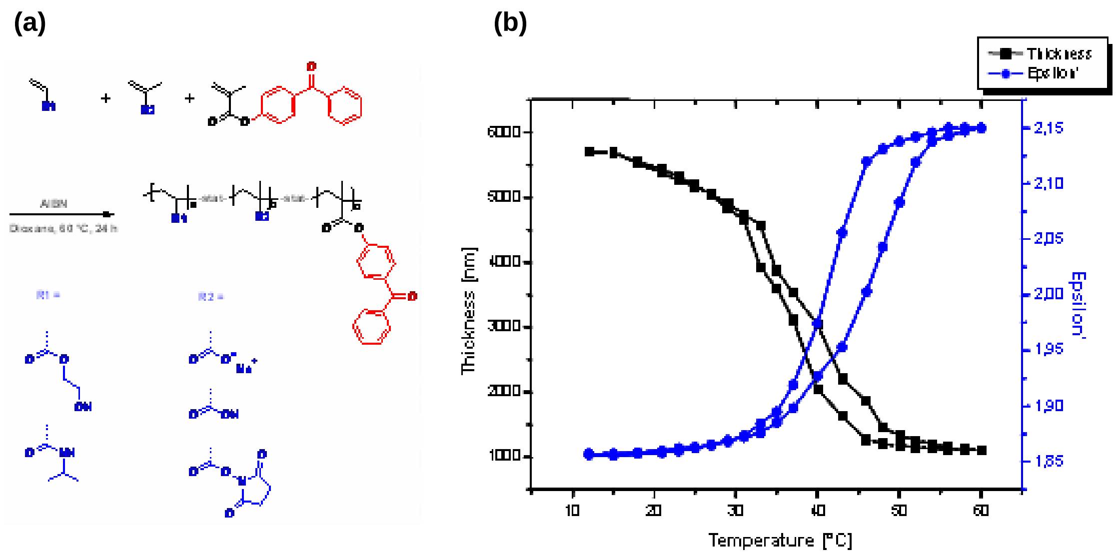

Figure 6. Synthetic scheme for adaptive polyelectrolytes, and the hydrogel response characteristics

Synthesis of (photolabile) Peptides

Control of the 3D nanoarchitectured surfaces will be controlled by the incorporation of 'designer' peptides that can respond to the environment. Figure 7 shows a control peptide system that has been synthesised that can respond to light. Such a system may prove useful in being able to write surfaces covered with peptides that can then bind other complementary peptide strands.

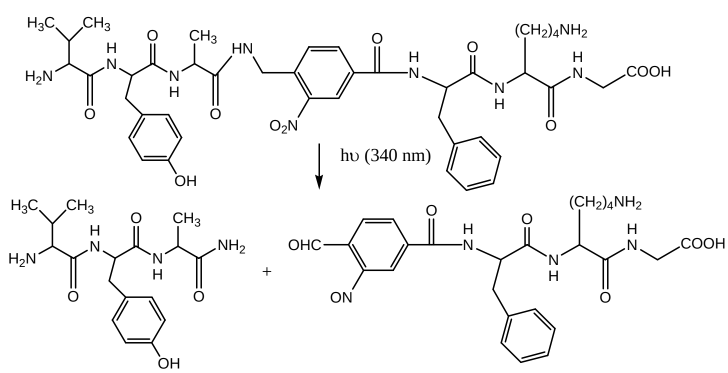

Figure 7. A photocleavable peptide

Synthesis of Inorganic and Organic Nanoparticles

Several approaches are being targeted for the synthesis of nanoparticulates. Of note are two novel approaches to nanorods. The first approach is the synthesis or ripening of gold nanoparticles in thermotropic discotic columnar liquid crystals that will direct the particle assembly along a uniaxial axis. The second approach relies upon wetting of a functional organic materials into nanoporous inorganic solids. This is achieved either from the organic melt followed by solidification or from solution followed by solvent evaporation. Figure 8 shows images of an organic nanorod formed from a polyfluorenyl derivative.

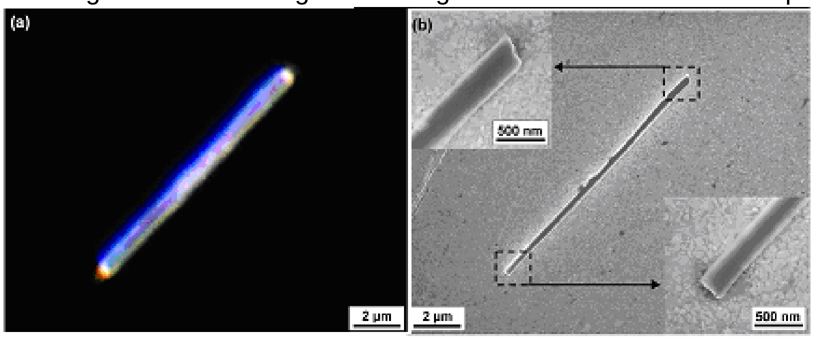

Figure 8. (a) epi-fluorescence and (b) SEM images of inorganic matrix templated polyfluorenyl nanowire.

Adaptive Surfaces

Quite fortuitously we discovered that a simple LBL system consisting of citrate passivated gold nanoparticles and a simple organic polycation could swell and de-swell (Figure 9a), which also had a transduction effect with respect to the manner in which the nanoparticles plasmon band coupled. Hence, whilst the sample was moist and the organic polycation was swollen with water, and hence keeping the particles far apart (d_1), the predominating feature of the visible spectra was the transverse band. However, upon drying and deswelling, whereby the interparticle layer distance decreases (d_2), the transverse bands couple giving rise to an enhanced longitudinal band. The process was reversible and hence may be used as a sensing transducer.

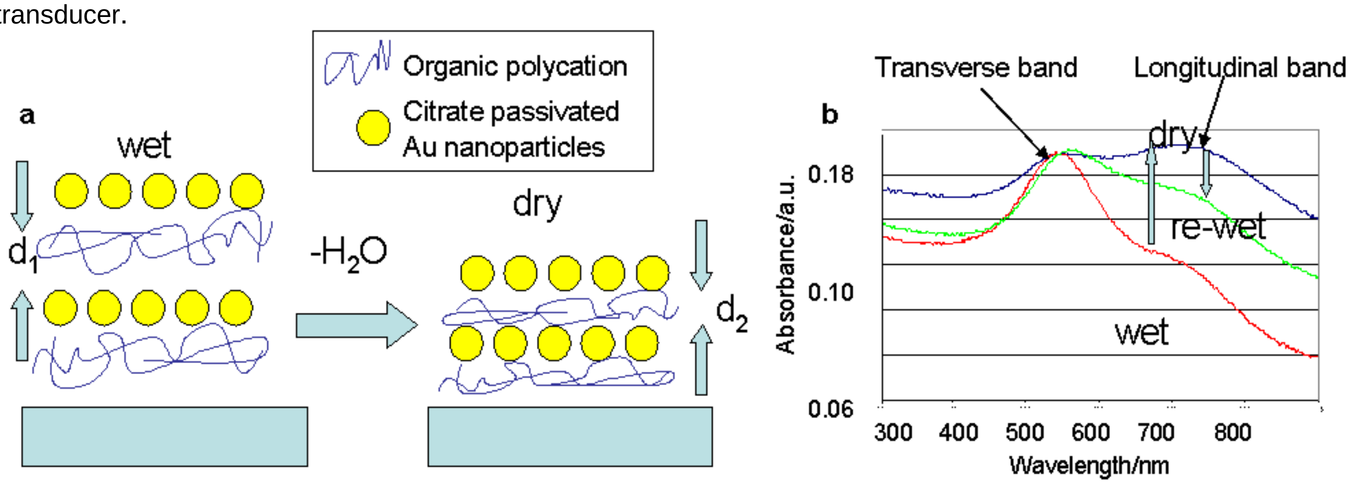

Figure 9. (a) Schematic of the swelling and deswelling process and (b) observation of the changes in the visible spectrum

Scale-Up

Ink-jet printing has been carried out by 9D on silicon substrates (prepared by TYN) of nanomaterials (UB), on both adsorbing and non-adsorbing surfaces, in order to assess the limits of the ink drop. It was concluded that this was compatible with the micron-length scale, and as such would potentially be a method for delivering nanoamterils to a nanopatterned array covering a micron scale area. In addition, the design of the microfluidic system for delivering reagents to the wafer is well-advanced.

Knowledge Dissemination Plan

The participants in the Nano3D consortia have given several lectures, both at national and international conferences, in which they have presented some of the results from the work carried out in the Nano3D project. Thus, several lectures across Europe have been given, but also further a field in India, South Africa and the US. These lectures have primarily been to the scientific community who are interested in nanoscience, nanoengineering and nanotechnology. In addition, other more general lectures have been given to a wider general audience, such as the IChemE and IMechE in the UK. After one year of research on the project, manuscripts are now in preparation, and the first papers will be submitted within 18 months of the scientific start of the project. The contents of the manuscripts will be/are scrutinized by each participant for patentable aspects.

Conclusions: Expected End Results and Impact

The overall objective of the research proposed in this document is to integrate top-down lithographic techniques which enable precise spatial patterning of surfaces from micron- to the nanoscale, with the controlled stepwise self-assembly and self-organisation of nanometer scale chemical and biochemical entities to these surfaces, to fabricate three dimensional (3D) adaptive nanostructured architectures, which have demonstratable uses, in a fashion that will allow the processes to be scaled into proto-type production methodologies.

The Nano3D consortia wish to be the first to demonstrate that nanostructures on surfaces can be created via an integration of top-down and bottom-up methodologies, by the self-organisation of self-assembled molecular building blocks on nanopatterned surfaces, such that the nanostructures are able to adapt to the environment. Furthermore, the Nano3D consortia wish to further innovate in illustrating that this approach can be scaled-up into a proto-type production process, such that automation and scaleability can be demonstrated. The Nano3D consortia will be innovating a new paradigm for manufacturing nanostructures on surfaces.

In addition, in response to the need for the transformation of industry towards higher-added value activities, one of the central outputs of the consortium is to develop new knowledge targeted towards high value-added technologies, including biotechnology, biomedicine and ICT. Successful innovations will ultimately enable new product and market development that will stimulate employment opportunities.