6th Framework Programme

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Instrument:	Specific Targeted Research Project

Final Publishable Activity Report

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Project coordinator name: Prof. Werner Blau

Project coordinator organisation name: The Provost Fellows and Scholars of the College of the Holy and Undivided Trinity of Queen Elizabeth near Dublin, (TCD)

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Publishable Executive Summary

General Overview of Project Objectives:

DESYGN IT started in September 2004 with the primary Scientific and Technical objective of this project is to establish Europe as the International Scientific Leader in the **De**sign, **Sy**nthesis, **G**rowth and Application of **n**anotubes, nanowires and nanotube arrays for **I**ndustrial **T**echnology. The DESYGN-IT consortium contains several of Europe's leading researchers in the nanotube and nanowire field. There are several high-tech SME partners who are well placed to assess the outputs of the project and benefit from the proposed research. Major contributions to the fundamental understanding of the synthesis, processing and properties of nanotubes, nanowires and arrays were confidently foreseen.

The scientific objectives of our work were to:

- Create know-how and encourage European Industry to be first to market with a cost effective mass production of high quality nanotubes i.e. make nanotubes accessible for European industry
- Reply to the demands of industry for low cost, high purity nanotubes and related products and in turn increase high-tech exports
- Demonstrate to industry the enhanced performance and cost benefits of nanotubes in their applications and provide the European industry with a practical understanding of the capabilities of nanosize materials
- Increase the number of publications and patents in the nanotube and nanowire field.

The main technical objectives of the DESYGN-IT project, in summary, were to

- Develop a low cost, clean process to produce high quality nanotubes
- Manufacture nanotubes with defined electronic and mechanical properties
- Provide nanotubes in a form that can be readily handled by industry
- Advance state-of-the-art in the development of metal and semiconductor nanowires
- Develop industrial prototypes for demonstration to industry; sensor device, SPM tip, actuator etc.

Work Performed and Results Achieved:

The ambitious objectives were addressed in an extended 40 month workprogramme executed over six technical workpackages. The work has resulted in many significant breakthroughs that have advanced the state of the art in a number of areas. In the body of this document, details of the work done in the project are given but the following is an overview of the major outcomes of each of the workpackages:

WP1: Large-Scale Synthesis of High Quality, High Purity Nanotubes.

- high quality and high purity carbon nanostructures (nanotubes and nanocages) were synthesised using new supercritical fluid deposition techniques that are potential nanomaterials for the large-scale fabrication of carbon nanotube-based devices.
- Bulk synthesis - more than 4 kg have been produced by Mo6 by end of 2007 and distributed to various users.
- Arc discharge CNTs found to be highly suited for use in melt blending of polymers and ink and screen printing applications.

WP2: Surface Engineering and Functionalisation of Nanotubes.

- Carbon nanotubes, with controllable dimensions and structures, were prepared as replicas from Fe-containing silica mesostructures.
- Gold nanoparticles to attached MoSIx wires and are inherently stable in air, compatible with Si-based technology, and can clearly be used as efficient one-dimensional connectors for molecular scale bottom-up circuit construction.
- Functionalised polymer molecules were grafted to nanotube surfaces.
- A patent application, for an improved method for producing reinforced polymer fibres, ribbons or films using arc discharge CNTs, has been filed. This technology has been used to make new super strong, conductive, magnetic and fluorescent polymer composites with a broad range of potential applications.
- Important steps towards the realisation of a bottom-up fabrication technology for complex structures, the ultimate goal in nanotechnology, realised with Programmed self-assembly work. The spin-off company nanoStructor was founded in 2007 based on this work.
- MoSI nanowires were shown to enable the amplified detection of cytochrome c using two possible routes. The new MoSI NW derived amplification bioassays are expected to open new opportunities for medical diagnostics and protein analysis.
- A significant scientific breakthrough in the synthesis of a novel FeMWNT composite material This should lead to new products and devices in a range of applications.

WP3: Controlled Growth of Nanowires and Nanoarrays.

- A parameter set was found to produce mechanically stable bucky papers with a two dimensional alignment of the nanotubes within the bucky paper.
- Plasma treatment can functionalize CNT powder, bucky papers and aligned CNTs but opening of aligned CNT was not achieved without damaging the tube shape.
- HBC derivative molecules offer a good molecular template from which to advance to complex mass self –assemblies (MSAs.). Research to tie-in optical measurements with electrical measurements will lead a general model to describe all the properties of the MSAs.
- MWCNT have been grown in-situ on W tips. Alternative methods such as using Ni tips were tested but reproducibility was poor.
- MWCNT and SWCNT on substrates were produced as films and arrays on substrates up to 2” in size. Field emission characteristics of the MWCNT and transistor characteristics of SWCNTs were tested. Further development of Nanoimprinting will enabled large scale lithography replacing electron beam lithography and provides higher throughput.
- CNT forests were dressed with Ag.

WP4: Characterisation of Nanotubes, Nanowires and Arrays.

- Specific procedures to characterise CNTs and MoSIx material with a range of applications. Work on nanomaterial characterisation within DESYGN-IT was published in a special edition of a nanotechnology publication.
- TEM SPM equipped with DC electrodes proven to be a valuable tool for systematic characterization of individual carbon nanotubes. Superior to lithography methods because of faster acquisition of results. This work has been used by a spin out company.
- TEM shows - Conductivity and field emission properties are nanotube structure dependent.
- Findings using the TEM-STM method show - critical current density of 7 10^6A cm^{-2} for iron filled CNTs with a diameter of 20-80 nm, the electron transport is diffusive., the electromigration process is reversible (an iron particle was picked up by electromigration and subsequently deposited on a surface).

- CNT coated glass samples were characterised optically and electrically and showed conductivity but the resistance level is in the MΩ range.
- A method to measure the absorption of low temperature laser produced plasmas was developed and the absorption of Ag plasma was measured. The results show that bound-bound transitions dominate the absorption and bound-free absorption is important in the UV.
- An automated procedure has been developed with a commercial Raman system and is now being applied within a national project to identify and age inks used in early manuscripts.
- Ag coated MWCNT are a highly effective SERS substrates with signal enhancements of the order of 10^9 By the appropriate selection of CNT length, the signal enhancement can be tuned to a particular laser wavelength. A number of joint publications are currently being prepared.

WP5: Development and testing of nanotube based actuator and nanotube reinforced polymer composites.

- Surface wettability of bucky papers changes by using the different plasma treatment. An instant wetting can be obtained after an oxygen plasma treatment, a slight increase in surface energy with oxygen-nitrogen mixtures, and a further increase with nitrogen plasma.
- Amorphous, semi-crystalline and block co-polymer carbon nanotube composites made by using a twin-screw extruder to disentangle nanotubes and disperse them in polymers.
- Carbon nanotubes dried upon glass can be electrical conductors. It is possible to spray on a coating with >80% transmittance but uniform electrically conducting coatings are difficult to achieve.
- MoSIx composites made with the highest conductivity measurements to date. Method for making CNT composites with high conductivity developed.
- Test rig developed in DESYGN -IT for measurements of Bucky Paper displacement, efficiency and the force generated.
- It was found bucky papers having a forest of aligned nanotubes grown on their surface have best actuation performance but low mechanical stability. SWNT and MWNT samples had next best actuation and their stability is higher. The displacement of bucky papers at higher potential inputs was confirmed and several actions can be taken get even greater displacement in the future.

WP6: Applications of Nanotubes and Nanoarrays: Prototype Devices and New Materials

- In displays, CNTs are an attractive new material with superior electrochemical properties, which could replace traditionally used counter electrode materials. Process issues resulting in low yields need to be solved.
- MWNT-tipped AFM probes offer higher lateral resolution and fewer tip convolutions than an all-silicon counterpart.
- With a CNT based electrode, one can generate DC low pressure plasma with about 30% less operating voltages and ~ 10^3 times more current. Controlling ballasting affects the CNT damage and the optimum conditions. Proposed mechanism - the plasma in the CNT based micro plasma device to be initiated with the help of field emission from CNTs.
- ZnO nanoneedles were grown as an electrode
- MWNT bucky papers with aligned nanotubes have good actuation but poor mechanical stability. Bucky paper from NMP dispersion has better mechanical stability and some actuation properties. Forrest of CNTs grown on stainless steel - low mechanical stability and some show actuation properties.
- A nanotube/nanowire based nanoelectromechanical (NEMS) device was demonstrated. An importance discovery with the nanorelay: with a high current through the Mo6I3S6 nanowire

conductivity increase five orders of magnitude due to re-crystallization of the wire-bundles and electromigration induced annealing of defects and interstitial impurities caused by the electron motion. MoSI wires can be used as intermolecular connectors and optimisation efforts lead to further improved conductivity, useful on the macroscopic scale.

- Gold coated carbon nanotube tips have been successfully used to enhance the light emission from an electron scanning tunnelling microscope (STM) tunnel junction.

Results of the Plan for Using and Disseminating the Knowledge:

The major DESYGN-IT results with immediate commercial value that members of the consortium have reported are:

- 2 spin out companies
- 7 patents granted
- 11 patent applications
- Plans for more patents applications
- Commercial negotiations with a company, outside of the consortium, to implement the technology of the project in a new product.
- Talks with one of the world's largest polymers companies, to exploit the DESYGN-IT results in a project to study Polyolefin CNT composites.

A summary of the dissemination activities that the partners in the consortium have participated in during the lifetime of DESYGN-IT are:

- More than 50 Conferences reaching academic and industrial audiences of between 60 - 10000.
- 8 Workshops reaching academic and industrial audiences of between 15 - > 250.
- More than 15 Exhibitions and Trade shows aimed at Industry with attendances of between 300 and 55000.
- 7 Press Releases
- 2 Newsletters and flyers
- 1 Video Clip released to the general public
- 6 Websites, with links to more than 50 websites hosting papers from the DESYGN-IT project
- Participating in 25 National and EU Collaborative Projects
- Members of 10 Policy and Standards group
- Funded the studies of 18 PhDs, 2 MSc, 5 Trainees and 4 Engineers

Website & Logo:

The project public website can be accessed through
http://www.tcd.ie/Physics/DESYGNIT/index.php

The logo, for the DESYGN project, has been developed for some time now; see above. This appears on all the DESYGN IT publishable material. It has been used on the following media: reports, slides, website, brochures and posters.

Project Objectives

General Objectives:

Nanotechnology provides a new approach to materials science and engineering and has the potential to be the flagship of the next industrial revolution. It is an enabling technology, which is already feeding into all sectors including electronics, pharmaceutical, IT and biotech.

Europe enjoys a strong position in the nanosciences and the potential is there to translate this expertise and know-how into a real competitive advantage for European industry. According to the *Derwent World Patents Index*, the US was awarded 2,716 nanotechnology-related patents between 1995 and 2001, while Asia earned 2,213 during the same period. Europe lagged behind with 1,873 published patents. Within the Asian region, Japan is the leading nation for patent output ahead of China and Korea. In Europe, Germany leads both France and the UK.

The aims of the EC Nanotech Programme in Priority Area 3 are to

1) *create an RTD-intensive European nanotechnology related industry*
2) *promote uptake of nanotechnologies in existing industrial sectors*
3) *generate a favourable climate for nanotech research*

DESYGN-IT clearly addresses the above aims and has a well defined ambitious set of scientific, technological and socio-economic objectives.

Nanotechnology research has come a long way in the past 40 years but the emphasis must be placed on development now. Transferring European outstanding nanotechnology expertise into industry and producing a high technology, knowledge intensive economy are essential now. In many sectors, European investment in R&D is considerably lower than either the USA or Japan. Figures released in the recent past indicated that the percentage of GDP invested in R&D in the EU-15 was less than half that of Japan and substantially lower than the percentage invested by the US. However, the investment situation is more positive for nanotechnology activities with government support for nanotechnology from the European Commission and EU member states increasing and according to figures from Ramon Compañó, a technology co-ordinator at the European Commission government support had reached €300M in 2001. Europe, with its many leading researchers in the nanotube field and recognized strong position globally, has been slow to pass the technologies into industry. Europe can build on this momentum, capitalize on past investments and make significant industrial progress in this area for the benefits of EU citizens.

This project has relevance in many applications across several sectors including transistors, interconnects, mobile applications, flat-panel displays, long-lasting batteries, sensors and composites, spintronics, photonics, ceramics and magnetic storage. Of great importance is the possibility to integrate nanotubes, nanowires and nanoarrays into sensor and diagnostic devices.

Current limitations regarding the manufacturing and application of nanotubes are not solely a European issue. The results from this project will offer a European solution to a global problem. Nanotube technology and knowledge is in demand worldwide.

Scientific objectives

The scientific objectives of the project are to:

- Create know-how and encourage European Industry to be first to market with a cost effective mass production of high quality nanotubes i.e. make nanotubes accessible for European industry
- Reply to the demands of industry for low cost, high purity nanotubes and related products and in turn increase high-tech exports
- Demonstrate to industry the enhanced performance and cost benefits of nanotubes in their applications and provide the European industry with a practical understanding of the capabilities of nanosize materials
- Increase the number of publications and patents in the nanotube and nanowire field.

Technical Objectives

DESYGN-IT brings together leading edge expertise in; nanotube and nanowire synthesis, surface engineering and functionalisation of nanotubes, the ability to align nanotubes on substrates and the identification of marketable applications. This project brings us closer to the integration of nanotubes in macrosystems. Each of the SME partners is a high tech company targeting high value niche applications and markets.

The technological objectives of DESYGN-IT are as follows:

- Clean synthesis of 'bulk quantities' of high purity and high quality nanotubes in a clean cost-effective process
- Controlled synthesis of nanotubes with chirality, diameter, length and predictable mechanical and electronic properties
- Synthesis and full characterisation of added-value surface engineered nanotubes
- Synthesis and application of nanotubes that are bioengineered and tailored-designed so as to accomplish detection of micro-organisms and biomolecules
- Synthesis and full characterisation of semiconductor and ferromagnetic nanowires
- Development of nanotube arrays on substrates such as silicon, glass or plastic
- Prepare a range of NT reinforced polymer nanocomposites by conventional polymer melt blending processes
- Application of nanotubes for use as scanning probe microscopy tips
- Create a working CNT actuator for use in pumps, valves, micro-robotics
- Demonstrate a nanoelectromechanical device
- Assess the use of nanotubes in display systems

Socio-economic objectives

The Socio-economic objectives of our work are to:

- Optimise the production of cost effective, high purity nanomaterials and added value products for European SMEs in order to increase European competitiveness
- Increase employment and skills development by creating job opportunities within the European nanotechnology sector and related high-tech industries
- Encourage trans-national and cross-sector exchanges between European SMEs thereby improving innovation capacity in traditional SMEs
- Enable SME intensive sectors, such as the manufacturing sector, to increase their market share and be first to market in niche areas.
- The knowledge generated in DESYGN-IT will be used to reduce the financial risk to SMEs in transferring nanomaterials into their industry

- Respond to National Nanotechnology Programmes and promote technology transfer between universities, research institutes, and SMEs

To address the ambitious objectives of DESYGN IT a work programme was defined with 8 work packages (WP) covering all areas of development of nanotechnology from synthesis of nanotubes to commercialisation of possible products and applications. There were 6 technical workpackages along with a workpackage addressing commercialisation and one dedicated to the management of DESYGN-IT. The technical workpackages addressed:

- Synthesis of Nanotubes
- Surface Engineering and Functionalisation of Nanotubes
- Controlled Growth of Nanowires and Nanoarrays
- Characterisation of Nanomaterials
- Development and testing of nanotube based actuator and polymer composites
- Applications - Prototype Devices and New Materials

The objective of each workpackage was:

WP1: Large-Scale Synthesis of High Quality, High Purity Nanotubes

To develop a process to manufacture high-quality nanotubes in high yield. Optimise existing nanotube production techniques, improve the yield and purity of the nanotubes obtained. All nanomaterials will be fully characterised as outlined in WP4, and distributed among the partners for use in all workpackages

WP2: Surface Engineering and Functionalisation of Nanotubes

To produce nanotubes with defined size, chirality and electronic properties. Refine reliable purification techniques, during and after synthesis. The resulting tubes to be surface-functionalised using plasma modification and chemical methods to add additional chemical groups to the tube outer in order to promote better interaction with polymer substrates. The addition of functional groups capable of interacting with micro-organisms is the first step in preparing a nanotube-based sensor device. All tubes will be characterised as in workpackage 4, with additional testing (e.g. electrochemical testing of bio-engineered tubes, ESR, tube purity measurements). After optimisation of the nanotube synthesis and surface treatment, the next stage is to investigate the scale-up of these processes.

WP3: Controlled Growth of Nanowires and Nanoarrays

Mesoporous materials have unidirectional pores with diameters in the range 2-15 nm and offer a convenient route to forming ordered arrays of nanowires. Mesoporous solids have previously been exploited as templates for semiconductor materials formed from the gas phase. Vertically aligned NTs prepared by Cambridge will be functionalised by Fraunhofer.

Methods of growing or aligning nanotubes (SW, MW and MoS2) on a range of substrates including glass, and silicon will be perfected and developed for applications in molecular sensing, scanning probe microscopy and glass technology. As part of this workpackage, nanotubes will be grown on tips for use in scanning probe microscopy.

WP4: Characterisation of Nanotubes, Nanowires and Arrays

To fully characterise all nanotubes, nanowires, bucky papers and arrays produced during the project, this WP runs from month 1 to 40, using such techniques as scanning electron microscopy (SEM/EDX), X-ray photoelectron spectroscopy, atomic force microscopy, BET-surface measurements, Raman spectroscopy, optical characterisation (visible and near infrared) of nanotube coatings on glass, TEM-STM, electrical testing and mechanical testing.

WP5: Development and testing of nanotube based actuator and nanotube reinforced polymer composites

Carbon Nanotube Sheets (Bucky Papers) will be investigated for their use as actuators. The investigation of the initial purity state as well as the Studies of the wetting of nanotubes will also be important for WP6. A test rig will be built to measure the response. Displacements of at least ~10nm with low power consumption of ~10 nW are expected. A series of conductive polymer nanocomposites reinforced with NTs will be prepared conventional melt blending equipment. Several types of tubes, including MW, MoS2 and functionalised, will be used, and the final polymer properties correlated with tube purity, electrical properties and the concentration of tube added to the composite. The composites' mechanical, electrical and barrier properties will be modelled and confirmed experimentally.

WP6: Applications of Nanotubes and Nanoarrays: Prototype Devices and New Materials

Nanotubes synthesised in workpackages 1 and 2, nanowires and arrays developed in workpackage 3 to be applied in industrial devices and applications. Prototype materials and devices to be constructed and tested under the guidance of SME partners. For example, NTera Ltd is commercialising applications of nanomaterials for the electronic display industry. The applications involve the use of high surface area electrodes and nanotubes are potentially useful in this regard. NTera and other development partners will manufacture the display application for the first time. The displays provide vastly superior optical properties than other display technologies. Specifically, the displays reflective properties approaching those of ink on paper and can be used in many areas where high levels of ambient sunlight prohibit the use of other technologies such as plasma, OLED, LED and LCD.

Contractors

Addressing the ambitious objectives of the project required a wide range of specialists and expertise. The DESYGN-IT project brought together 14 partners, including several of the leading European researchers in the nanotube and nanowire field and seasoned experts who have participated in FP4 and FP5 Programmes. The multidisciplinary consortium includes chemists, physicists, engineers and commercialisation specialists. Each of the research partners in this consortium has long standing research programmes in nanotube/nanowire technology, and each is internationally recognised for innovation in their field. Bringing researchers, SMEs and entrepreneurial researchers who have already spun out companies together in one project has driven this research forward towards exploitation in industry.

List of Participants

Participant				
Name	**Lead**	**Expertise**	**Short name**	**Country**
Trinity College Dublin	Prof. Werner Blau Prof. James Lunney	Project co-ordinator, nanotube synthesis. Laser ablation	TCD	IRL
National University of Ireland, Cork	Dr. Justin Holmes	SCF processing and nanotube filling	UCC	IRL
Institute Josef Stefan	Prof. Dragan Mihailovic	Synthesis of MoS2 nanotubes	JSI	SI
University of Ulster	Dr. Pagona Papakonstantinou	Bioengineering of nanotube surface	UU	UK
Queen Mary College	Dr. Mark Baxendale	Nanotube filling, molecular electronics	Queen Mary	UK
Queens University Belfast	Dr. Paul Dawson Dr. Tony McNally	Raman spectroscopy, SERS Polymer nanocomposites, modelling	QUB	UK
Fraunhofer	Dr. G. D. Weiss Dr. Uwe Vohrer	Actuator technology Surface analysis, plasma treatment	Fraunhofer	DE
University of Cambridge	Prof. Bill Milne	Synthesis of CNT arrays	UCAM DENG	UK
Toughglass Ltd	John Agnew	Manufacturer of bent safety glass for special applications	TG	UK

Participant				
Name	**Lead**	**Expertise**	**Short name**	**Country**
Sensor Technology & Device Ltd	Prof. James McLaughlin	Application of sensor technology	ST&D	UK
Mid Sweden University	Dr. Hakan Olin	Scanning probe microscopy	MSU	S
NTera Ltd	Dr. David Corr	Developer of display applications.	NTL	IRL
Mo6 B.V	Erik Wijnen	Commercialisation of new nano-materials based on transition metal chalcogenides	Mo6 B.V.	NL
University of Latvia	Dr. Donats Erts	TEM-SPM	UL	LV

Co-ordinator Contact Details:

Principal Investigator: Prof. Werner Blau
Address: SNIAM, Physics Dept.,
Trinity College Dublin,
2 College Green,
Dublin 2,
Ireland.
Phone: + 353 (1) 6081708
Fax: + 353 (1) 6082151
Email: wblau@tcd.ie

Work performed and results

With the DESYGN-IT project handling such a range of disciplines, the responsibility for directing and reporting the progress of all the tasks in a workpackage was assigned to one partner. This was the partner with the most technical or industrial experience in the area tackled in the work package. The progress on DESYGN-IT has been steady, and a number of significant breakthroughs have been made. In-depth results of DESYGN-IT are given in the reports delivered during the lifetime of the project. The deliverables and their dissemination level are given in the following table.

No	Title	Nature	Level
D1.4	Production of pure, well graphitised nanotubes	D1.4.1: Samples D1.4.2: Tech. description	RE CO
D1.2	D1.2.1: 100 g of TMC material based on Mo, S and I within 12 months.	D1.2.1.1: Samples D1.2.1.2: Report	RE CO
	D1.2.2: 100 mg of doped MoSIx NW material. Characterisation of their properties and quality control	D1.2.2.1: Samples D1.2.2.2: Report	
D1.1	50g of high quality nanotubes produced by SCF	D1.1.1: Samples D1.1.2: Report	RE CO
D1.3	1 kg quantities of NW material	D1.3.1: Samples D1.3.2: Report	RE CO
D2.3	Application of SCF to produce NTs with controllable structure and size	D2.3.1: Samples D2.3.2: Report	CO
D2.5	Fabrication of gold-Nan particle terminated nanowires. Fabrication of functionalised MoS NWs and evaluation of their characteristics by microscopy	D2.5.1: Paper	PU
D2.8	Fabrication of polymer functionalised nanotubes and molecular bridging of nanotubes	D2.8.1: Paper	PU
D2.6	Definition of possible self-assembly routes of Mo-S NWs for large-scale integration	D2.6.1: Report	CO
D2.2	D2.2.1: Post-synthesis separation of nanotubes by conductivity type as evidenced by Raman spectroscopy and direct electronic measurement	D2.2.1.1: Report	CO
	D2.2.2: Post-synthesis separation of nanotubes by band-gap energy as evidenced by Raman spectroscopy and direct electronic measurement	D2.2.2.1: Report	
D2.4	Electronic transduction of biological binding events on CNT surfaces	D2.4.1: Report	CO
D2.7	D2.7.1: MWNT sample (mg quantities) with 100% filling of central capillary with fcc Fe	D2.7.1.1: Samples, D2.7.1.2 Report	CO
	D2.7.2: SWNT sample (mg quantities) with 100% filling of central capillary with fcc Fe	D2.7.2.1: Samples, D2.7.2.2 Report	
D2.1	Contact-to-contact growth of nanotube of a single conductivity type by translation vector selection	D2.1.1: Report	CO
D3.6	Evaluation of the optimum alignment techniques for nanotubes	D3.6.1: Sample D3.6.2: Tech. Description	CO
D3.2	Functionalised vertically aligned nano tubes	D3.2.1: Samples D3.2.2: Report	CO
D3.4	Fabrication of self assembled nanowires.	D3.4.1: Paper	PU
D3.3	Demonstrate procedure for contacting nanotubes with reproducible contact resistance	D3.3.1: Report D3.3.2: Demonstration	CO RE
D3.8	FIB machined tip precursor structures report and sample. Tip structures with metal-coated or metal filled CNT tip elements.	D3.8.1: Sample D3.8.2: Report	RE
D3.5	D3.5.1 CNT Field emission cathodes fabricated using PECVD and ECR-CVD routes	D3.5.1.1 Report D3.5.1.2 Sample	CO
	D3.5.2 Arrays of SWCNT FET's	D3.5.2.1 Report D3.5.2.2 Sample	
D3.7	Preparation of metal (Ag or Au)-coated nanotube arrays	D3.7.1: Sample D3.7.2: Report	RE
D4.5	Field emission properties correlated with microstructure of nanotubes	D4.5.1: Report	RE
D4.4	Conductivity properties correlated with microstructure of SCF grown CNT and of arc discharge grown CNT	D4.4.1: Report	CO

No	Title	Nature	Level
D4.6	Electromigration properties of filled nanotubes	D4.6.1: Report	CO
D4.3	Analysis of the CNT coated sample for Toughglass application	D4.3.1: Data D4.3.2: Report	CO RE
D4.1	Chemical, optical, mechanical and electrical characterisation of nanotubes and products	D4.1.1: Report D4.1.2: Data	RE
D4.9	Analysis of laser-induced plasma emission using LIBS	D4.9.1: Report D4.9.2: Paper	CO
D4.8	Demonstration of a commercially exploitable Raman technique for user-friendly characterization of SWCNT materials	D4.8.1: Report D4.8.2: Data	CO RE
D4.2	Observation of high-sensitivity SERS signal on nanotube-based substrates	D4.2.1: Report	CO
D5.1	Selection of the optimum electrolyte for wetting of nanotubes	D5.1.1: Data D5.1.2: Tech. Description	RE
D5.4	Synthesis of polymer carbon nanotube composites by melt mixing	D5.4.1: Samples D5.4.2: Report	RE CO
D5.5	Manufacture of CNT composite sprayed onto curved and flat glass	D5.5.1: Samples D5.5.2: Report	RE CO
D5.7	High conductivity MoSI polymer composites	D5.7.1: Samples D5.7.2: Report	RE CO
D5.6	Correlation of extrusion processing conditions and the mechanical, electrical and barrier properties with the nanostructure of polymer nanotube composite materials	D5.6.1: Paper	PU
D5.2	Formation of buck paper actuating device	D5.2.1: Report D5.2.2: Prototype	CO RE
D5.3	Results of actuation and electrical properties of SWNT buck paper	D5.3.1: Report	RE
D6.6	Samples of CNT films prepared by screen-printing process	D6.6.1: Report D6.6.2: Device D6.6.3: Electrode	CO RE CO
D6.1	Collection of SPM images using nanotube-based tips.	D6.1.1: Report D6.1.2: Demonstration	PU RE
D6.5	Produce a low turn on voltage source for use in a microplasma sensing device	D6.5.1: Report D6.5.2: Device	CO CO
D6.7	Appropriate test methods for devices based on intended field of use	D6.7.1: Report D6.7.2: Report/Method	PU CO
D6.4	Results of actuation properties of buck paper actuator	D6.4.1: Report D6.4.2: Demonstration	RE RE
D6.3	Demonstration of a nanoelectromechanical device	D6.3.1: Report D6.3.2: TEM movie	CO PU
D6.8	Diagnostic hardware suitable for online monitoring of CNT coating application	D6.8.1: Report D6.8.2: Report	CO
D6.2	Enhancement of optical output from STM using metal-coated nanotube tips and/or substrates	D6.2.1: Report	CO
D7.1	Book of specifications	D7.1.1: Report	RE
D7.2	Technico-economic assessment	D7.2.1: Report	RE
D7.3	D7.3.1: Costing and environmental audit of current manufacturing.	D7.3.1.1: Report	RE
	D7.3.2: Commercial application assessment of Mo-S NW materials	D7.3.2.1: Report	
D7.6	Website to promote project results	D7.6.1: Website	PU
D7.4	Commercial assessment of NTs in battery and display applications.	D7.4.1: Report, D7.4.2: Demonstration	PU
D7.5	Consortium commercialization meeting	D7.5.1: Minutes	CO
D7.7	Workshops to showcase emerging technologies, new products and devices	D7.7.2: Book of abstracts	PU
		D7.7.4: Book of abstracts	
D8.4	Project presentation	D8.4.1: Presentation	PU

No	Title	Nature	Level
D8.1	Mid-term reports	D8.1.1: Mid-term	CO
	Final reports	D8.1.2: Final	
D8.5	Final plan for using and disseminating knowledge	D8.5.1: Report	CO
D8.2	Exploitation plan	D8.2.1: Report	CO
D8.3	Final report on deliverables achieved	D8.3.1: Report	CO

Where the dissemination levels are defined as:

- PU: Public
- PP: Restricted to other Programme Participants (including the Commission Services)
- RE: Restricted to a group specified by the consortium (including the Commission Services)
- CO: Confidential, only for members of the consortium (including the Commission Services)

What follows is a brief description from each of the DESYGN IT partners of their achievements in the project.

TCD

In task 1.4 of the project, scaled-up arc-discharge production of CNTs was carried out by TCD on a Kratschmer-Huffman Generator. Production parameters were optimised to produce very strong, very straight, thermally stable CNTs. They are considerably more temperature stable than CNTs produced using CVD. However, as can be seen in the plot below, the production yields are in general poor while purity can be as low as 10% with the rest of the carbon in the form of species such as turbostratic graphite and carbon onions.

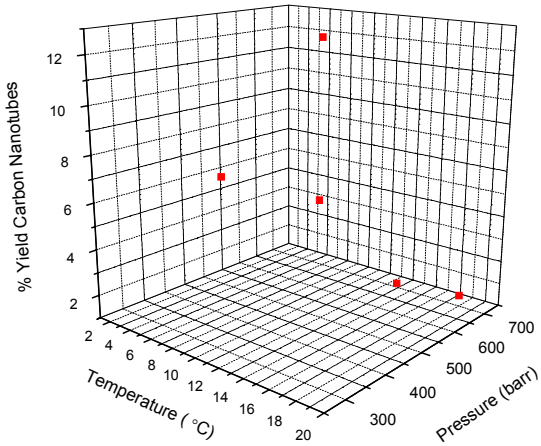


Figure 1: % Yield of Nanotubes as a function of varied production parameters, temperature and pressure.

Purification methods such as oxidation can be carried out the CNTs but these affect the structural integrity of the nanotubes which is essential for many mechanical and electrical applications. Thus, the ability to mass-produce well graphitised, high quality nanotubes depends on an improvement of the arc discharge production method.

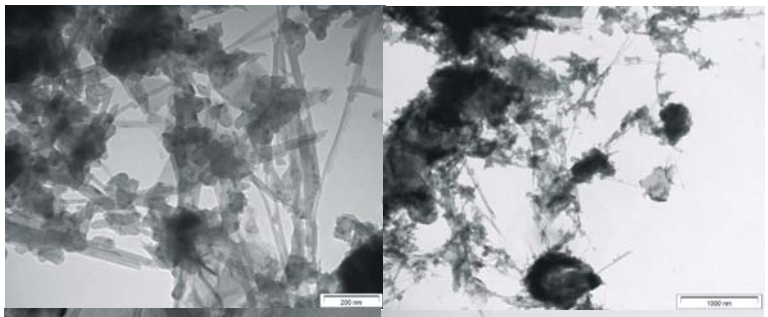


Figure 2 -TEM images of MWNT soot **Before Purification**

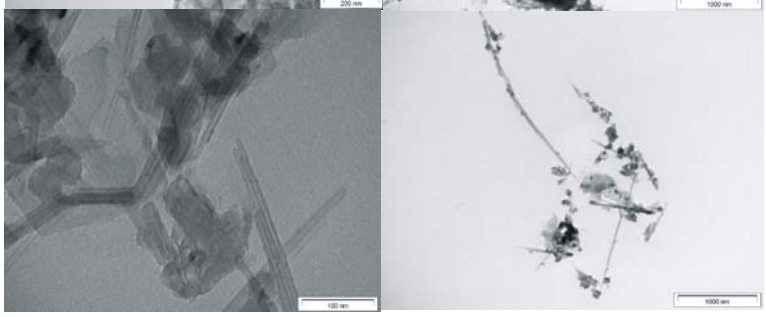


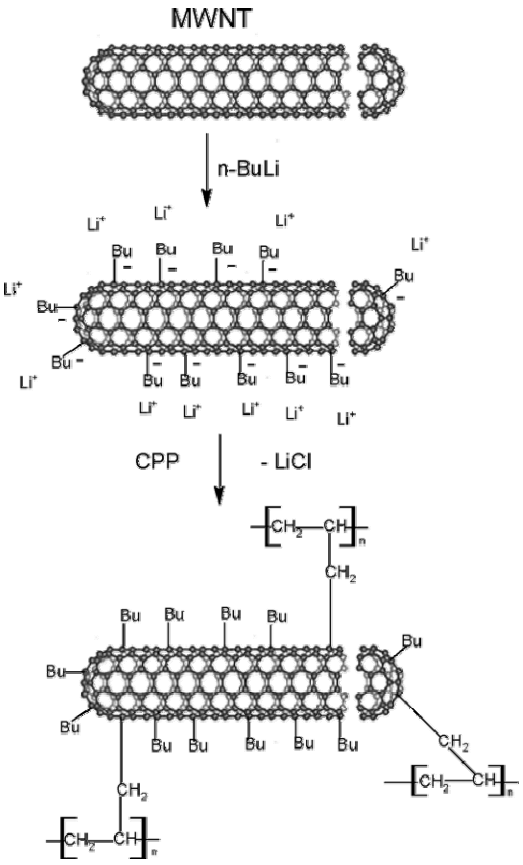
Figure 3 TEM images of MWNT soot **After purification**

These difficulties are reflected in the limited number of CNT suppliers in the marketplace opting for this method of production. Out of fifteen marketplace leaders in the supply of CNT's

only one third offer CNT's produced using arc discharge as a method of production, (eight suppliers choosing the CVD method). Despite the poor yield from this method of CNT production, there may well be commercial grounds to scale up and optimise the process for specific applications. Within the project, it has become quite clear that CNTs produced by arc discharge are highly suited for use in melt blending of polymers and ink and screen printing applications

In 2.8. TCD worked on CNT Functionalisation and Molecular Bridging. Covalent functionalisation and surface chemistry of single-walled carbon nanotubes have been envisaged as very important factors for CNT processing and applications. Due to the relatively smooth graphene like surface of nanotubes, there is a lack of interfacial bonding between polymer matrix and CNTs. Nanotubes, in particular SWNTs, are typically held together as bundles resulting in poor nanotube dispersion in polymer matrices. Chemical functionalisation of the CNT surface is expected to resolve these problems. Two main strategies for the covalent grafting of polymers to the nanotubes have been achieved: ''grafting from'' and ''grafting to''.

The ''grafting from'' method is based on the initial immobilization of initiators onto the nanotube surface followed by the in situ polymerization of appropriate monomers with the formation of the polymer molecules bound to the nanotube. The advantage of this technique is that polymer–nanotube composites with quite high grafting density can be prepared. However, this method requires a strict control of the amounts of initiator and substrate as well as a control of conditions for polymerization reaction.



The ''grafting to'' approach is based on attaching already preformed end-functionalised polymer molecules to functional groups on the nanotube surface via different chemical reactions. An advantage of this method is that preformed commercial polymers of controlled mass and distribution can be used. The main limitation of the ''grafting to'' technique is that initial binding of polymer chains sterically prevents diffusion of additional macromolecules to the surface leading to low grafting density. Also only polymers containing reactive functional groups can be used. An example of the ''grafting from'' strategy is a treatment of SWNTs with sec-butyllithium that generates carbanions on the nanotube surface. These carbanions serve as initiators of anionic polymerization of styrene for in situ preparation of polystyrene-grafted nanotubes. This procedure allows the debundling of SWNTs and produces homogeneous dispersion of nanotubes in polystyrene solution. As detailed in Scheme, MWNTs have been functionalized using n-butyllithium and then covalently bonded to a chlorinated polypropylene.

The following addition of the polymer-grafted nanotubes to the chlorinated polypropylene polymer matrix resulted in significant increase of mechanical properties. As nanotube content is increased to

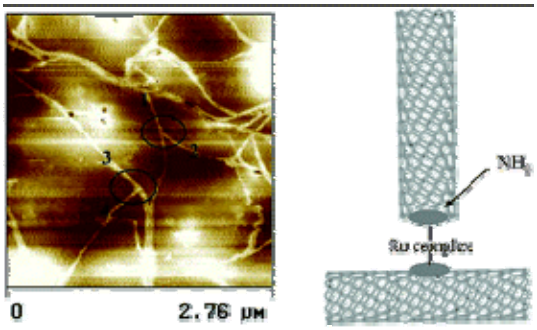


Figure 4 - AFM images of CNT bridges.

0.6 vol %, Young's Modulus increased by a factor of 3, while both the tensile strength and the toughness increased by factors of 3.8 and 4, respectively. This covalent functionalisation enables us to get an efficient dispersion and excellent interfacial stress transfer, leading to new ultra-strong polymer composite materials.
Intermolecular CNT bridges were formed through amide linkage of amino functionalized MWNTs and [Ru (dcbpy)(bpy)2](PF6)2, an inorganic metal complex. Interconnects were visualized using atomic force microscopy, see Figure. 4

Absorption and emission spectroscopy showed significant changes between starting products and the resulting ruthenium nanotube complex, indicative of successful chemical bridging.

Two particularly interesting CNT polymer composites were investigated by TCD in the final year of the project; Artificial Spider's Silk and Fibres and Ribbons from e.g. Kevlar

For the silk-like material, we chose the synthetic spider silk, Biosteel. Functionalized nanotubes were chosen, with the nature of the functionality determined by the requirement that both nanotubes and Biosteel be soluble in the same solvent. We produced composite films based on Biosteel, with a range of CNT mass fractions by solution processing and drop casting. These films were then investigated using tensile measurement to assess potential mechanical reinforcement. Increases in stiffness, strength, ductility and T were observed at very low CNT loading levels. **The rate of increase in stiffness with volume fraction shows extremely good polymer CNT stress transfer.**
Blond, D.; McCarthy, D. N.; Blau, W. J.; Coleman, J. N. Toughening of Artificial Silk by Incorporation of Carbon Nanotubes Biomacromolecules; 2007; 8(12); 3973-3976.

With the CNT material produced by arc discharge from DESYGN IT, **an improved method for producing reinforced polymer fibres, ribbons or films by swelling them in a nanoparticle suspension under various conditions was found. The method provides the ability to modify any preformed polymer fibres ribbons or films by a simple and cost effective swelling procedure. This technology has been used to fabricate new super strong, conductive, magnetic and fluorescent polymer composites with a broad range of potential applications**. The polymer used is not particularly limited as long as the polymer can be produced in the form of yarns, fibres, fabrics, ribbons or films. The polymer is preferably a polyamide, such as a Kevlar, which is not soluble in the most of common solvents, but can be easily swelled in n-methyl pyrollidone (NMP) or dimethylformamide (DMF). **PCT application has been made.WO2007010517** Publication date: 2007-01-25 Inventors: Gounko Iouri Kuzmich; Hayden Hugh; Coleman Jonathan Nesbit; O'Connor Ian Edward; Blau Werner Josef; Blake Rowan

Four different methods to make electrical contact to nanowires and nanotubes have been compared by TCD in task 3.3. Each of the methods has its own advantages and disadvantages. Both the casting and the beam deposited methods involve only a few processing steps and so enable the properties of the wires to be quickly measured. Electron beam lithography enables short wires (< 1 µm in length) to be contacted to and different metals to be used. The *in-situ* micromanipulation method enables

complicated wire architectures to be prepared, for example wires to be crossed and overlaid and to be placed onto systems onto which it is not possible to spin photoresist.

A good strategy for the progressive analysis of simple molecular self assemblies (MSAs) has been identified in task 3.4. Discotic HBC molecules were compared with small structural variations and a deeper understanding of the fundamental physics behind MSAs was achieved. The development of the exciton-aggregate model for macromolecules was a key step, as it will help apply what has been learnt from HBC MSAs to future, more complicated, MSAs. In TCD's case, knowledge of the photo-physics of HBC-C8,2 and HBC-PhC 12 in turn helped decipher the more complicated behaviour of the N-HBC MSA.
Thus, HBC derivative molecules offer a good molecular template from which to advance to complex MSAs. The differing properties of the three kinds of MSAs investigated, offer enough scope to continue research with a view to implementing them as nanodevices.

Ongoing research in TCD is focusing on the electrical properties of the MSAs and their interconnectivity in inert polymer matrices. The aim is to tie-in optical measurements with electrical measurements and in so doing arrive at a general model to describe all the properties of the MSAs above. Another avenue for examining MSAs in the future will be to use a known, simple MSA as a local probe to investigate MSAs that are more complex. In other words, MSAs will become the nanotools of the future. It is therefore necessary, for the development of NT, to research the fundamental physics behind MSAs.

TCD developed specific procedures to characterise CNTs and MoSIx material with a range of applications. The following is an overview of the work done:
Microscopy
SEM analysis was performed a range of samples provided by the partners, including ink with CNTs, nanoarrays and bucky papers. High resolution TEM was performed on MoSix. AFM was specifically used to determine the size distribution. The group at TCD produced stable dispersions of single-walled carbon nanotubes using the surfactant sodium dodecylbenzene sulfonate. Atomic force microscopy analysis was used to determine bundle diameter distribution of the nanotubes exfoliated on dilution of these dispersions.
Opticalspectroscopy
An automated procedure has been developed with a HORIBA Jobin Yvon labRAM HR, a commercial Raman system, for measuring Raman spectra. A new technique was applied to the analysis of SWNT – using an NIR spectrometer; the Fluorescence map of a range of materials was measured.
Mechanical Analysis
Thermal stability on different environments is routinely determined using TGA. DSC is used to measure crystallinity in composites and to determine the influence of CNTs and MoSix on the polymer environment.
Electrical Measurements
The contact resistance of the samples of individually contacting nanotubes produced in task 3.3 were measured and dc and ac analysis of composites was carried out.

In task 5.7, we looked at conductivity of MoSIx composites and CNT composites. Unlike CNTs, MoSIx nanowires exist as one electronic type (all metallic), are dispersible in common solvents and tend to debundle in solution. This makes them ideal candidates as conductive fillers.
In task 5.7, we have measured alternating current (AC) and direct current (DC) conductivity as a function of volume fraction for composites of Mo6S4.5I4.5 nanowires in PMMA, produced by solution

processing. The Mo6S4.5I4.5 nanowires are highly conducting and form a percolation network with a very low threshold of pc = 1.3 × 10 -5. ***This appears to be the lowest threshold measured to date for any one-dimensional conductor/insulator composite system. The highest conductivity measured was 4 × 10 3 S/m, which is high enough for anti-static applications.***
We went on to develop a technique to make free standing films by drop-casting a solution of composite dispersions with either carbon nanotubes or carbon nanodisks as fillers, in standard weighing boats. The nanotube films have high conductivities of ~500 S $m^{-}1$, illustrating their more homogeneous nature. Such films, when fabricated from single-walled nanotubes, tend to be porous but display high conductivity, indicating good electrical contact between nanotubes. These nanotube films can be thought of as a high volume fraction percolative network where the polymer matrix has been replaced by air. This means that no resistive barriers are present and good electrical connection is expected at nanotube junctions. This is confirmed by the high film conductivity.

In Task 4.9, a method to measure the absorption of low temperature laser produced plasmas was explored. Pulsed laser irradiation (1064 nm, 6 ns) of a Ag target at a laser fluence of 1 J cm^{-2} was investigated. This is important as an in depth knowledge of the laser ablation conditions will benefit the pulsed laser deposition of Ag nanoparticles as carried out in WP 3.5. The absorption of Ag plasma was measured and a value of 0.5 – 1.5 x 10^{-17} cm^{-3} was found for the absorption cross section in the visible region. Calculations using the FLYCHK spectroscopic code correlate well with experiment. The calculations show that bound-bound transitions dominate the absorption and bound-free absorption is important in the UV. The discrepancy between the experimental data and the code predictions can be attributed to limitations within FLYCHK. It will be of interest to extend these measurements to the UV and IR region and to perform these studies as a function of laser fluence. Another extension of this work would be to measure the expansion and deposition of ablated material to examine if the optical absorption during the laser pulse affects the plasma much later in time. The extension of this work is being carried out by the TCD group.

In WP 3.5, Ag and Au nanoparticles were deposited by Pulsed Laser Deposition (PLD) on polymer and glass substrates and were studied by TEM and optical absorption spectroscopy, at TCD. It was found that ultra thin films (>5nm) are structured on the nanometre length scale and have interesting photonic applications The UV-Vis absorption spectra of the samples showed that the Surface Plasmon Resonance (SPR) peak occurs in the region of 400-500nm for Ag nanoparticles and 550-650 nm for Au nanoparticles. It was found that the SPR feature depends strongly on the nanoparticles size and shape, the resonance increases in magnitude and peak wavelength with increasing nanoparticle size and a double resonance occurs for nanostructures that are rod shaped. Finally, to gain some theoretical insight into the optical properties of nanostructured metals the effective medium theory of Maxwell Garnett was used and showed it can be used to calculate the main features of the optical absorption.
PLD of Fe, Co and Ni nanostructures has led to interest for possible catalytic growth of other materials. Nanostructured films of these metals were grown and these samples were used by UCAM-DENG as catalysts for CVD growth of CNTs. Initial results (AFM, SEM and Raman) show that nanotube growth takes place and that Fe seems to be the best catalyst.
Nanosphere lithography (NSL) has also been used in conjunction with PLD to produce a deposition mask for the production of ordered arrays of nanoparticles. At present, uniform arrays of up to 50 square microns have been produced. It is desirable to have a uniform coating over a much larger area and so a surfactant has recently been added to the nanosphere solution, to aid in the coating of these arrays. NSL was also used with thermal evaporation to produce ordered arrays and was also found to work well.

UCC

105 g of purified multi-walled and single-walled carbon nanotubes, grown by chemical vapour deposition (CVD) and supercritical fluid (SCF) deposition methods, have been supplied to the other partners (UL, MSU, Fraunhofer, Toughglass, NTera). The multi-walled carbon nanotubes supplied also include bamboo-structured and nitrogen-doped carbon nanotubes. The purity of the carbon nanostructures supplied was > 90 %.

A number of catalysts (Fe, Co, Ni, Pd), supports (MgO, Al2O3, SiO2) and carbon sources (ethanol, xylene, acetylene, methane) were tested for growing high yields of well graphitised multi- and single-walled carbon nanotubes by CVD. The best multi-walled and single-walled carbon nanotubes produced by CVD was by the deposition of methane over MgO supported Co/Mo catalysts at 900°C. Nitrogen-doped multi-walled carbon nanotubes have also been prepared by chemical vapour deposition. Acetonitrile, ethylenediamine, and ammonia were used as nitrogen sources.

We reported for the first time a continuous-flow SCF method for growing carbon nanotubes with high selectivity, up to 80 % of the carbonaceous materials formed was multi-walled carbon nanotubes, and in high yield, up to 100 % compared to the amount of catalyst used. In our experiments, supercritical carbon monoxide (sc-CO) was used as the carbon source for generating the carbon nanotubes over MgO supported Co/Mo catalysts at 750 °C. Carbon monoxide was chosen as the carbon source as it has been successfully used as a gaseous reactant, at relatively low pressures, to generate high quality carbon nanotubes (yields less than 8 %) by the HiPco process. However, the SCF process developed in this project is fundamentally different from the HiPco method in which CO is used as a gaseous reactant and not in its supercritical state. The structural properties of the carbon nanotubes produced from sc-CO were characterised by scanning and transmission electron microscopy (SEM and TEM), thermal gravimetric analysis (TGA) and Raman spectroscopy.

In summary

SCF deposition technique employing sc-CO has been shown to be an efficient method for the large-scale production of MCNTs. The high concentration of sc-CO used in the reactor results in a remarkably high yield of nanotubes. The diameters of the multi-walled nanotubes synthesised ranged from 10 to 20 nm, with lengths of several tens of micrometres. The SCF grown nanotubes also exhibited field emission characteristics similar to CVD grown multi-walled nanotubes (Figure 1).

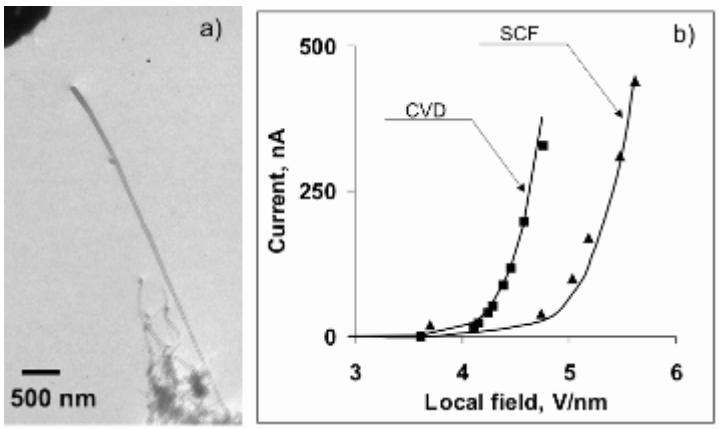


Figure 1. (a) A typical TEM image of a SCF-grown nanotube used for field emission measurements (length = 5.5 μm and radius ≈ 10 nm); (b)field emission current of the SCF grown multi-walled nanotubes (triangles), field emission current of a multi-walled nanotube grown by CVD method (rectangles) and fitting using the Nordheim-Fowler fit (line) as function of local field.

These results suggest that SCF-grown nanotubes are potential nanomaterials for the large-scale fabrication of carbon nanotube-based devices. *Co and Fe clusters supported on mesoporous silica (SBA-15) and Y-type zeolite supports were also studied as catalysts for multi-walled carbon nanotube growth in supercritical CO and CO2.*

Carbon nanocages, with remarkably large mesoporous volumes, were also synthesised by the deposition of p-xylene over a Co/Mo catalyst in supercritical carbon dioxide. Nanocages with diameters ranging between 10 to 60 nm were synthesised at temperatures between 650 to 750°C. The surface area and pore volume of the nanocages produced was found to depend on the reaction temperature and pressure employed. In particular, carbon nanocages with a pore volume of up to 5.8 cm3 g^{-1} and a BET surface area of 1240 m2 g^{-1} were readily synthesised at a temperature of 650°C and pressure of 10.34 MPa (Figure 2). The high pore volume and surface area of the carbon nanocages synthesised makes them ideal materials for use as inert adsorbents and catalytic supports. 10 g of carbon nanocages produced by a SCF deposition method have been supplied to other partners for testing (UU, Fraunhofer).

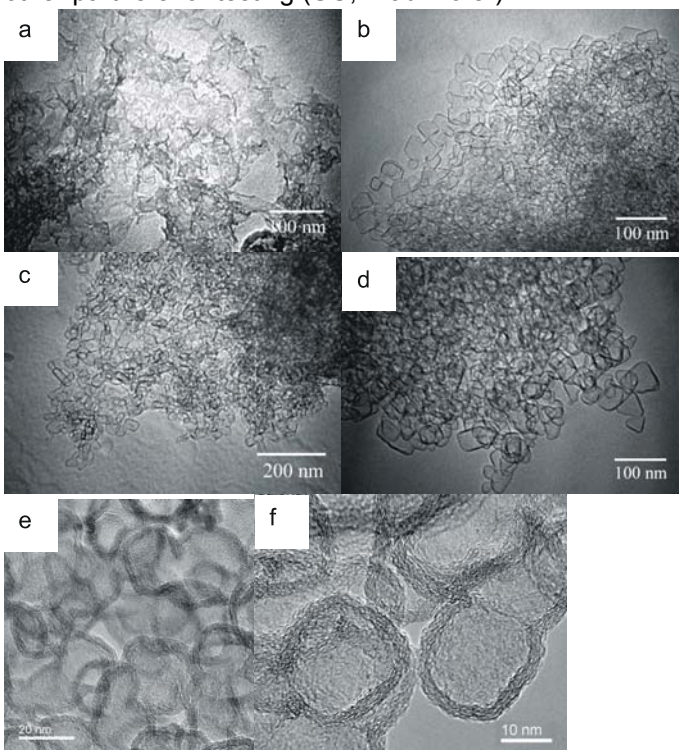


Figure 2 TEM images of carbon products prepared using sc-CO_2 on Co/Mo/MgO at (a) 600 ^{o}C, (b) 650 ^{o}C, (c) 700 ^{o}C, and (d) 750 ^{o}C. (e, f) HRTEM images of sample (c) reveal curved carbon layers. Molar ratio: p-xylene/CO_2=0.4%, Pco_2=10.34 MPa.

Bamboo-structured carbon nanotubes (BCNTs) with narrow diameter distribution were synthesized on bimetallic Cu-Mo catalysts. The diameters of the carbon nanotubes were approximately 20 nm, with lengths of several microns and wall thicknesses between 3–5 nm. The catalytic nanoparticles, with a mean diameter less than 20 nm, played a key role in the synthesis of the nanotubes, acting as nucleation seeds for growth. Raman and thermal gravimetric analysis results showed that the quality of the BCNTs was dependent on the amount of Cu present in the catalyst. ***These results challenge accepted wisdom that significant yields of CNTs can only be formed from catalytic CVD routes if 1st row, mid-row transition elements are used as catalysts***.

Carbon nanotubes were successfully prepared as replicas from Fe-containing silica mesostructures deposited inside the channels of anodised aluminium membranes (AAMs). Due to the confinement imposed by the channels of the AAMs, rather unusual mesophase structures showing “circular” and “columnar” mesoscopic channels were formed that were replicated, using SCF deposition technique, as pure carbon analogues after removal of the templating hosts (Figure 3). Raman data collected on nanotubes produced showed a well defined G-band confirming the presence of sp2 carbon type structures present within the wall of the nanotube framework. The appearance of a further broad Raman signal at 1350 cm-1 indicates a certain degree of disorder in the CNTs. There are many causes for this disorder which include deformation of the tube walls during HF treatment and replication of the silica structure, as well as the inability of the Fe catalyst to completely convert non-organised or glassy carbon to graphitic structures. The carbon nano-filaments obtained were assembled in the form of macroscopic membranes and may find applications as innovative materials for high surface area carbon electrodes, catalyst supports and further templates for more elaborate metallic nanostructures. Our results may offer some new insights into the structure and size control of CNTs, which at present is proving to be an illusive endeavour.

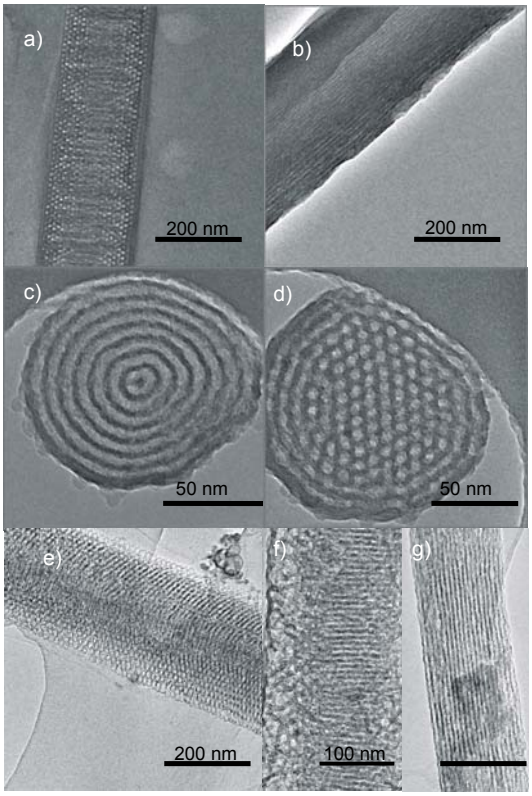


Figure 3. TEM images of the Fe-containg silica mesostructured nano-filaments with a) “circular” and b) “columnar” channels, c) and d) the corresponding TEM images of the filaments inside the pores of an AAM, and TEM images of isolated carbon replicas with e) and f) “circular” and g) “columnar” mesopores

IJS

In task 2.5 MoSIx nanowires were successfully functionalized with gold nanoparticles and proteins. The functionalisation of $Mo_6S_3I_6$ nanowires with gold nanoparticles is shown in figure 1.

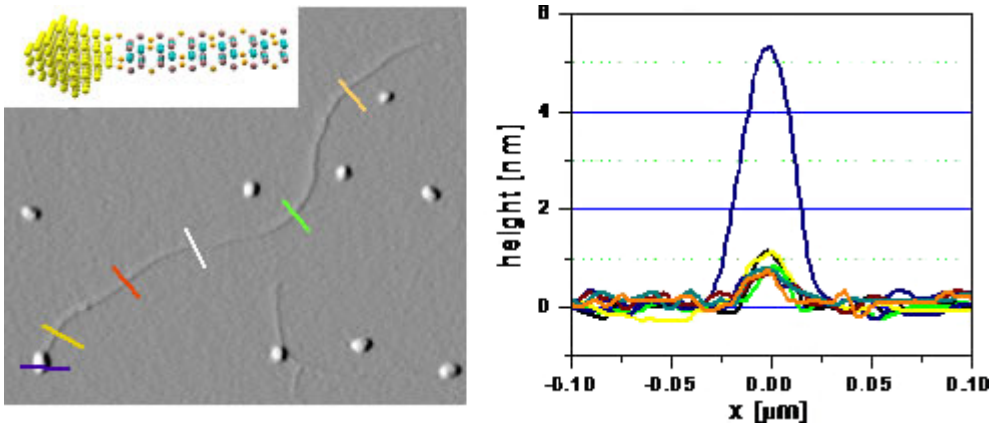


Figure 1: Left - AFM image of the 1 nm nanowire with a 5 nm gold nanoparticle at the end. Right - the height cross sections across the gold nanoparticle and the nanowire at different positions. Colour code applies for the positions of cross sections.

The attachment of gold nanoparticles was done in solutions. 5nm colloidal gold in water from BB International with starting gold chloride concentration of 0.01% was used. The functionalized nanowires were investigated under AFM. The attachment of gold to the bundles in water solution had a yield of up to 60%.

To test the assumption of covalent bond between Au atoms and S atoms, we tried to attach silver nanoparticles (20 nm nanoparticles from BB International). The silver nanoparticles did not attach to nanowires or thin bundles as was expected.

Functionalisation of $Mo_6S_3I_6$ nanowires with protein thyroglobulin was very successful. First, we attempted to attach thyroglobulin to a nanowire or a thin bundle through a gold nanoparticle, which was successful. From that study, we learned that the thyroglobulin can attach itself directly to the nanowire as shown in figure 2.

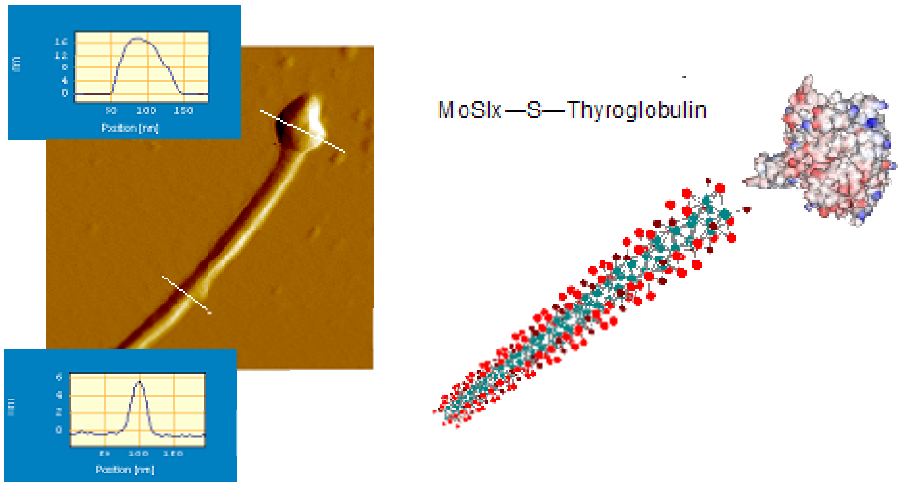
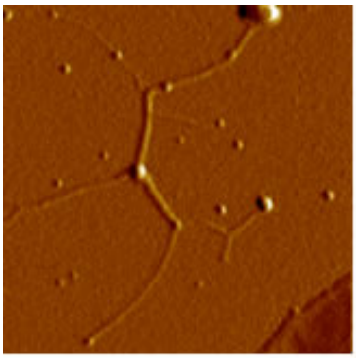


Figure 2: On the left is an AFM image of the 5 nm thin bundle with a protein thyroglobulin at the end. On the right is a schematic representation of the attachment.

In conclusion, we can say that ***functionalisation of nanowires with gold nanoparticles or proteins, which have –SH groups present on the surface works pretty well. From the analysis of the collected data, we can with a good degree of certainty assert that the bonding is covalent***.

In the task 2.6, we built on from the work on the task 2.5, where we found out that three nanowires can be attached to a single gold nanoparticle. It was evident that the functionalized nanowires can assemble into arrays. The nanowires on the nanoparticle encompass 120° angle and can hence arrange themselves into arrays as shown in the figure 3.

AFM image of MoSIx nanowires attached to 5 GNPs



Equivalent “circuit”

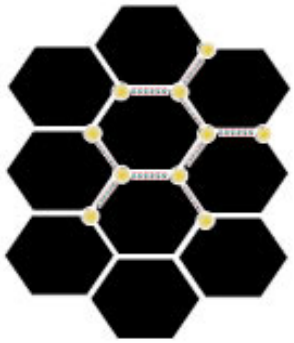


Figure 3. AFM image of a nanowire array and a drawing of an equivalent circuit.

Self assembly of MoSIx nanowires and DNA has been investigated. Disulfide-modified oligonucleotides A25 that are commercially available from Operon (Fig. 4) were mixed with the MoSIx nanowires in a buffer solution. As was indicated from the work on the task 2.5, a direct connection by S-S bond can be formed to the nanowire if -SH groups are present on the DNA...

Figure 4. A schematic representation of disulfide-modified oligonucleotides A25 with 25 bases

The nanowires that were functionalized with DNA strands were removed from the buffer solution with centrifugation. The solution that contained residual non-attached DNA was discarded while the sedimented nanowires were dispersed in fresh water. The process of centrifugation and dispersion in fresh water was repeated four times. In each step, we investigated the obtained solution of dispersed nanowires and the solution of non-attached DNA with UV-Vis spectroscopy. After the last centrifugation we could not resolve a characteristic peak of disulfide-modified oligonucleotide A25 at around 280nm from noise any more in the discarded solution, while the peak was clearly present (Fig .5) in the solution with dispersed nanowires, indicating the attachment of DNA.

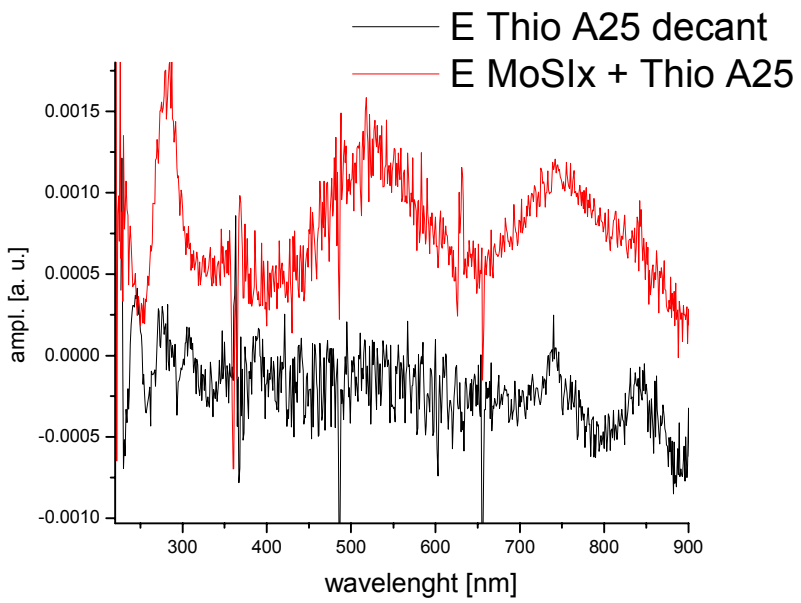


Figure 5. UV-Vis spectra of the solutions in the last step from which the MoSIx nanowires were sedimented out with centrifugation (black line) and the dispersed nanowires that have attached DNA.,

Unfortunately, the confirmation of the attachment of A25 under AFM was not possible because the A25 strands were too short to be successfully identified with AFM.

In the task 4.1 a collection of different investigations on basic properties of molybdenum-sulphur-iodine nanowires was done. The investigations range from structural studies to studies of mechanical, transport and optical properties. The structure was studied with combination of experimental techniques that included X-ray powder diffraction measurements (XRD), X-ray absorption fine structure experiments (XAFS), atomic pair distribution function analysis (PDF), high-resolution transmission electron microscopy (HRTEM) and scanning transmission electron microscopy (STEM). The experimental techniques were complemented with first principle calculations. The investigation of optical properties included measurements of reflectivity and absorbance on either mechanically orientated thin films, bulk samples or in solutions. The studies of mechanical properties were done under the AFM. The collected data was published in a number of scientific articles.

UU

In task 4.1 Plasma functionalisation studies on vertically aligned carbon nanotubes were performed. UU employed angle- and temperature-dependent NEXAFS spectroscopy to study the electronic and structural properties of highly oriented MWCNT treated with pure N plasma using low-pressure rf-PECVD route at room temperature. Interestingly, the N K edge spectra of CNx nanotubes showed that majority of the N atoms were introduced as substitutional graphitic nitrogen with small percentages incorporated in a pyridinelike structure and cyanic structure. This is in contrast to studies on directly grown nanotubes in nitrogen atmosphere, where the majority of nitrogen atoms were introduced in pyridine sites. Angle-dependent NEXAFS studies confirmed that the vertical alignment of nanotubes is preserved after plasma treatment (figure 1). ***This opens an avenue for functionalisation, where the conservation of vertical alignment is important (e.g., nanoelectronic applications)***. The O K edge NEXAFS and XPS spectra revealed that the oxygen functionalities were substantially improved after N-plasma treatment. Low-pressure rf plasma treatment is an effective route on introducing nitrogen atoms on the hexagonal lattice; however, it leaves the surface with very high reactive sites capable of adsorbing oxygen. Thermal gravimetric analysis measurements revealed a lower decomposition temperature for the plasma treated carbon nanotubes, which has its origin in the presence of a large fraction of active sites induced by rf glow discharge plasma treatment that accelerates the oxidation rate of N-doped carbon nanotubes ***Our results indicate that rf low-pressure glow discharge- mediated doping of nanotubes is a promising route to control the electronic structure of nanotubes and their reactivity due to introduction of active site defects. We envisage that rf glow discharge could be a route for implementing nanotubes, in gas sensor applications.*** The results from this study have been published in Phys Rev B (G. Abbas et al Review B 75 (2007) 195429.

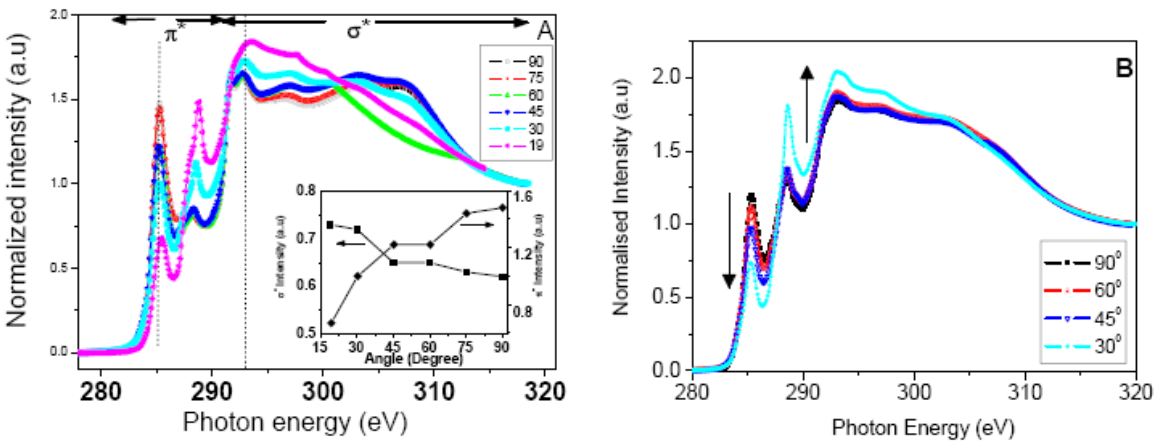


Figure 1. The Angular dependence of the normalized NEXAFS spectra of (a) pristine and (b) N-doped CNTs samples at the C K- edge. The inset of Fig. (1a) illustrates the intensities evolution of π * and σ* resonances with the incidence angle (ϕ)).

In this task, the changes in the first and second order Raman spectra of multiwalled carbon nanotubes (MWNTs) functionalized with oxygenated groups were also studied. The oxygen groups were introduced onto the nanotube surface through two strong acid purification routes: (1) reflux in concentrated (70%) HNO3 acid for 4 h at 80 °C and (2) ultrasonification in 3 HNO3 (70%):1H2SO4 (98%) for 8.5 h. Raman spectroscopy, using two laser excitation wavelengths (514.5 and 632.8 nm), x-ray photoelectron spectroscopy, and thermal gravimetric analysis were employed to study the evolution of the products. All the techniques revealed a higher degree of functionalisation for scheme 2 compared to scheme 1. Charge transfer phenomena were manifested by a shift of the C1s core

level towards higher binding energies. We found that the intensity of both the D and G energy Raman modes if normalized to the second order mode D* mode follows similar trends upon acid treatments. ***This result together with the observed dispersion of G mode can be interpreted as an indication that the G mode in carbon nanotubes is defect induced in a double resonant process. Both acid schemes cause an upshift of D and G Raman modes, due to intercalation of acid molecules, exerting pressure on the sp2 structure and an electron transfer from the pi states in MWNTs to the oxygen atoms.*** The results of this study have been published in Journal of Vacuum Science and Technology B (H. Murphy et al J. Vac Sci. Techn B. 24 (2006) 715)

The performance of glassy carbon (GCE) and graphite pencil electrodes (PGE) modified with multiwalled carbon nanotubes (CNTs) have been compared based on the direct electrochemical detection of nucleic acids in task 4.2. This was accomplished by monitoring the differential pulse voltammetry changes of the guanine signal. CNT-modified PGE compares favourably to that of the commonly used CNT-modified GCE owing to the intrinsic improved performance of the supporting PGE. The better intrinsic characteristics of the PGE are related to its composite structure and higher level of porosity compared to GCE. The performance characteristics of the direct DNA hybridization on the disposable CNT-modified PGE are studied in terms of optimum analytical conditions such as probe concentration, target concentration, hybridization time and selectivity (figure 2). ***The new DNA biosensor has shown some important advantages such being inexpensive, sensitive, selective and able to generate reproducible results using a simple and direct electrochemical protocol. The detection limit was estimated as 1.6 10-8 mol/L.*** The results of this study have been published in Analytical Chemistry (E. Erdem et al, Analytical Chemistry, 78 (2006) 6656).

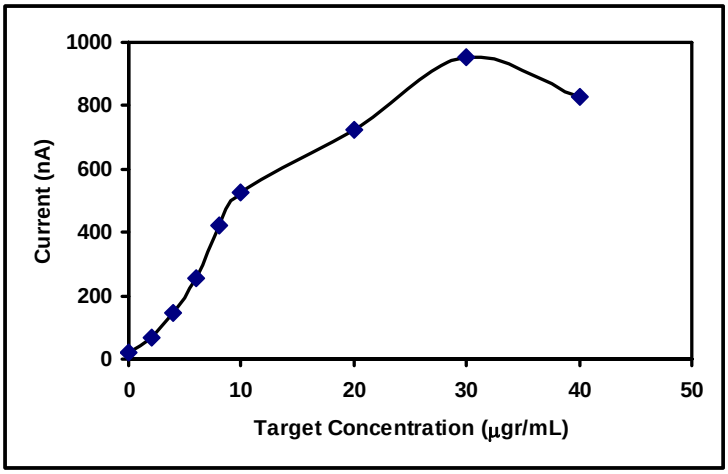


Figure 2. Plot showing the changes of guanine oxidation signal obtained by using probe immobilized onto CNT modified graphite pencil electrodes and different concentrations of target from 2 to 40 μg/mL.

UU demonstrate that Mo6S9-xIx nanowires (MoSI NWs) enable the amplified detection of proteins with cytochrome c as a model protein using two distinct routes: (i) electrochemical impedance spectroscopy (EIS) and (ii) UV-vis spectrometry. The EIS amplification is attributed to the formation of a negatively charged nano-interface upon association of the nanowires to the gold electrode. The protein binding reverses the surface charge leading to switching from repulsion to attraction of the redox [Fe(CN)6]3-/4- marker and to a sensitive label free EIS detection (figure 3). Heme proteins were also detected optically in the presence of a MoSI NWs solute through UV-vis amplification effects. The association of cytochrome c with the nanowires was verified by scanning electron microscopy, X-ray photoelectron, light scattering and micro-FTIR spectroscopes. ***Our results show that MoSI NWs is a promising nanostructure for the development of ultrasensitive sensors for detecting protein.***

The new MoSI NW derived amplification bioassays are expected to provide a straightforward and effective strategy for protein analysis and biosensor construction. The results of this study have been submitted to a refereed Journal

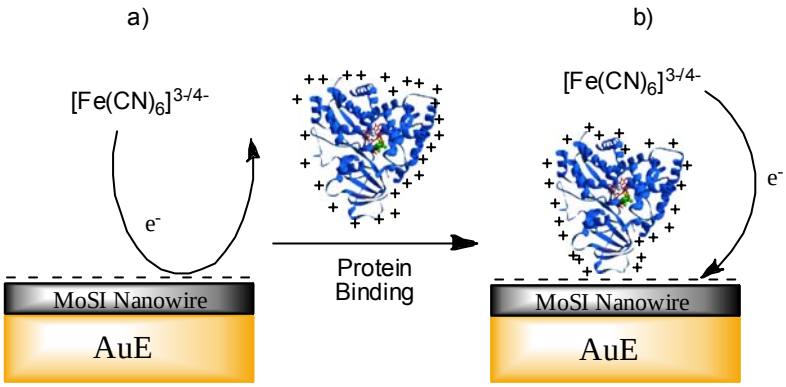


Figure 3. Mechanism of the label-free EIS biosensing of cytochrome c at the MoSI NWs modified AuE. Without the target protein the negatively-charged [Fe(CN)6]3-/4- marker is repelled from the surface and its redox reaction is hindered (A). When the protein binds to the MoSI NWs, the [Fe(CN)6]3-/4- marker is attracted to the surface and the electron transfer resistance decreases (B).

In task 3.5 Fe catalytic growths of open ended tubular graphite cones and low threshold field emission properties were examined. Large-area tubular graphite cones (TGCs) with an open end were successfully synthesized on Si substrates by microwave plasma assisted chemical vapour deposition using a thin Fe film as catalyst. As-grown TGCs have a through hollow nanotube core and an open tip. Some of them are very sharp with an apex angle as small as 2 − 3°. (figure 4). The Fe catalyst was clarified to only locate in the root, strongly supporting the catalytic base-growth mechanism. Their field emission performance exhibits a turn-on field as low as 1.8 V/μm. ***The present study will open the way to site selective growth of this unique TGCs and demonstrates its potential use in the drug delivery and cold cathode.*** The results of this study have been submitted to a refereed journal

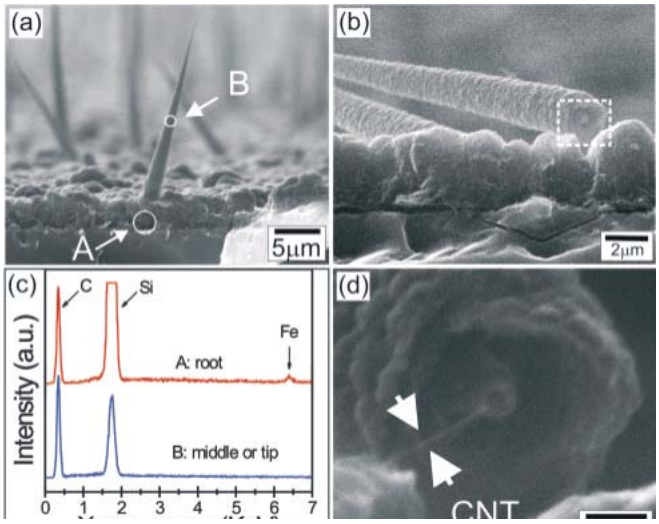


Figure 4. (a) and (b) Cross-sectional SEM image of the TGC sample; (c) EDS spectra taken from of the root and middle of individual TGCs shown in (a); (d) Enlarged image of the marked area in (b), showing a CNT in the TGC.

Queen Mary

Queen Mary was involved in WP2, WP3, WP4, and WP6. The main outcome of WP2 was the growth of milligram quantities of SWNTs and MWNTs filled with the ferromagnetic phase of Fe. MWNT-filling was achieved by pyrolysis of a C_{60} and ferrocene mixture; the product being a self-organised thin film comprising aligned filled-MWNT structures (see figure below). SWNT-filling was achieved by impregnation of purified SWNTs with $FeCl_3$ solution and subsequent heat treatment.

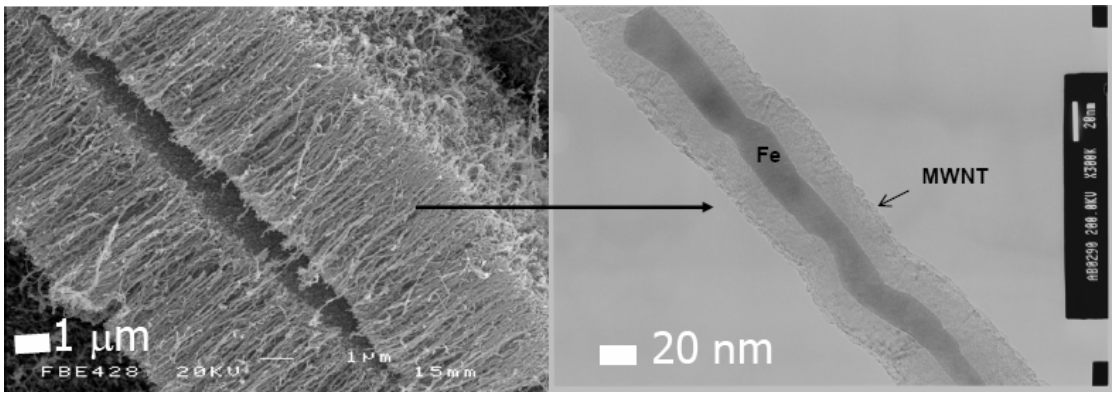


Figure 1: SEM image of self-organised thin film growth of aligned Fe-filled MWNTs produced by pyrolysis of C_{60} and ferrocene (left); TEM image of an individual Fe-filled MWNT.

Fe-filling of nanotubes adds magnetic functionality to the impressive range of mechanical, electronic and thermal attributes of the unfilled MWNT structure. Mössbauer spectroscopic and magnetisations studies confirmed the presence of the ferromagnetic phase of Fe in the nanotube core.

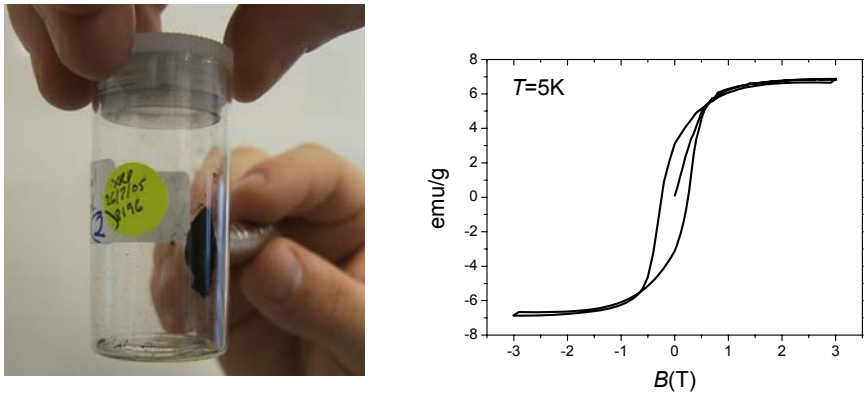


Figure 2: attraction of Fe-filled MWNTs to permanent magnet at room temperature (left); ferromagnetic hysteresis in the magnetisation of a Fe-filled MWNT film (right).

Several applications followed from this successful synthesis. **Firstly, the QM involvement with collection of SPM images for WP6 prompted consideration of Fe-filled MWNTs for magnetic force microscopy (MFM).** The external field distribution for a Fe-filled MWNT (FeMWNT) approximates to a magnetic monopole hence ultimate MFM resolution could be offered by a probe based on a vertical FeMWNT. The principle of this advantage relative to conventional MFM probes is illustrated below. Other advantages of the FeMWNT MFM probe are: i) the Fe core of a FeMWNT probe is chemically passivated by the MWNT shell which also serves as ii) protection against friction damage.

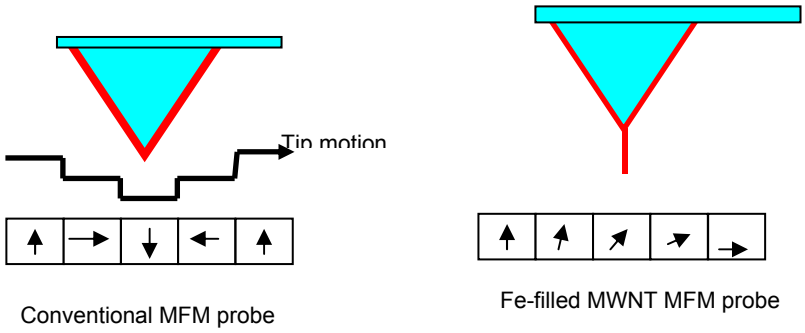


Figure 3: the principle of FeMWNT-based MFM probe: tip convolutions from a conventional probe (left) are overcome by the tip geometry offering the possibility of improved resolution of domain boundaries (right).

FeMWNT MFM probes were fabricated using a Co-coated AFM probe and an electrical pick-up method (see figure below). The FeMWNT extension to the probe was adhered to the tip by depositing amorphous carbon at the interface using a high SEM beam current. A successful attachment rate of <10% was achieved. Initial tests of the FeMWNT MFM probe revealed comparable topographical performance relative to a conventional MFM tip but inferior sensing of magnetic force. To optimise the magnetic response an attachment method capable of >10% efficiency is required. This work is ongoing beyond the end of DESYGN-IT; we are confident that high-resolution MFM can be achieved by this method.

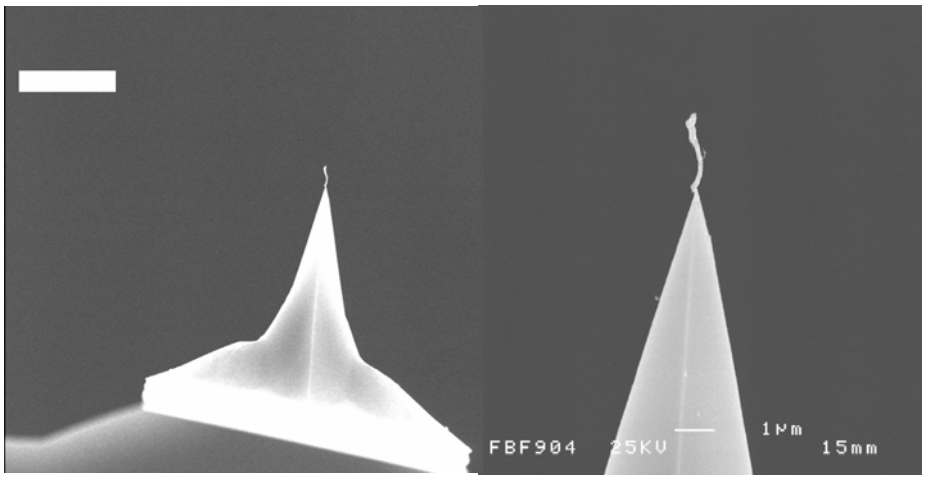


Figure 4: SEM images of a Co-coated AFM probe with FeMWNT extension.

The second FeMWNT application pursued under DESYGN-IT was a polymer/FeMWNT composite material; this followed from a fruitful collaboration with colleagues involved in "INTELTEX" (Contract number: 026626-2). This collaboration produced a MWNT/polyurethane-urea composite with universal strain vs. resistance characteristics (R. Zhang, M. Baxendale, T. Peijs, Phys. Rev. B 76, 195433, 2007). A composite from the same system but with 10 wt.% FeMWNT loading was prepared in the latter stages of DESYGN-IT, the rationale was again to add magnetic functionality. The above-percolation limit FeMWNT loading give a conductive, elastic, composite material that also exhibited a strong lateral magnetoresistance vs. strain response (see figure below). The FeMWNT loading of this prototype composite is by no means optimised yet ~70% magnetoresistance for *B*=0.1 T applied perpendicular to a stained ribbon on material was achieved. The origin of the magnetoresistance is undoubtedly incremental strain due to the perpendicular

magnetic forces on the strained ribbon. The magnetoresitance and magnetically induced perpendicular motion point to applications in which a remotely driven membrane with feedback signal is required, such as a valve for regularizing irregular fluid flow.

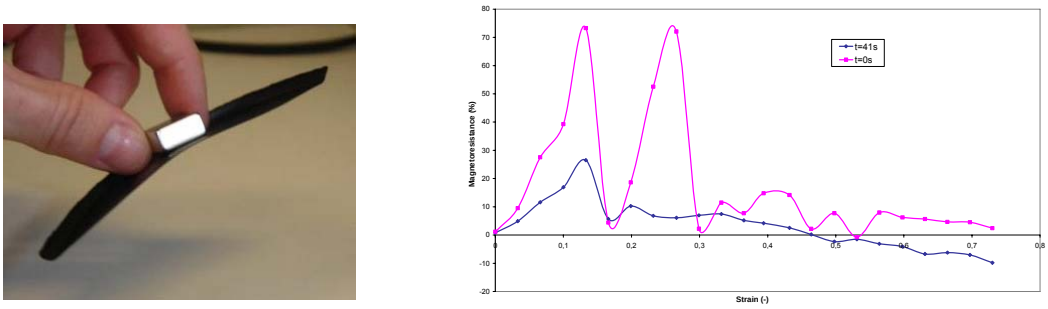


Figure 5: 10 wt.% FeMWNT/polyeurethrane-urea composite material (left) and magnetoresistance vs. strain for a perpendicular magnetic field *B*=0.1 T (right).

QM activity in WP4 centred on electronic characterisation of nanotubes. Samples were obtained from consortium members and external suppliers were characterised using a novel break-junction technique outlined in the publication: M. Baxendale, M. Melli, Z. Alemipour, I. Pollini, T.J.S. Dennis, J. Appl. Phys. 102, 103721, 2007. Quantum electronic transport information was obtained for a statistically large number of nanotubes in units of the quantum of the conductance G_0. The information yielded by this method was feedback to those consortium members involved in nanotube/polymer work. The main achievement of this work was the interpretation of statistical conductance data as in the example histogram below. The *y*-axis parameter is a measure of the frequency of occurrence of the *x*-axis value of conductance for a statistically large number of conductance measurements performed on networks of nanotubes. The theoretically predicted peak at $2G/G_o$ for a SWNT network was observed as illustrated below. **The outcome of this work was a model for interpretation of the other integer and fraction peaks on the conductance histograms for SWNTs, simple models for double- and multi-wall nanotube conductance, and data concerning the effect on electronic transport of covalent and non-covalent functionalisation of nanotubes (papers on these themes are in preparation with partners QUB and MSU).**

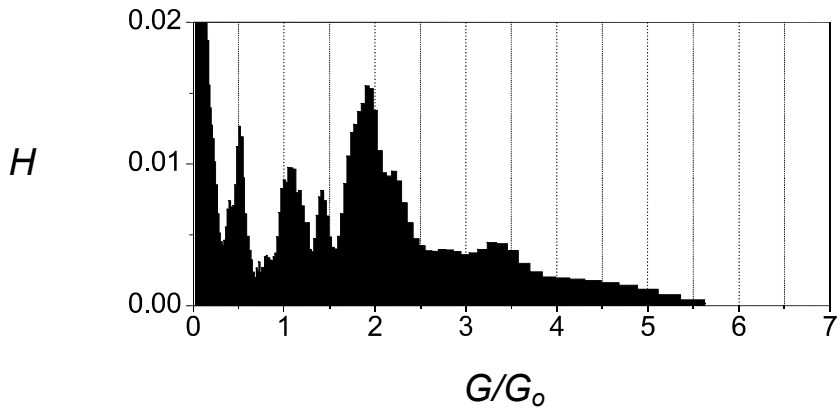


Figure: quantum conductance histogram for a SWNT network, the parameter *H* is a measure of the frequency of occurrence of the *x*-axis conductance value (expressed on units of the conductance quantum G_0). The theoretically predicted peak is at $2G/G_o$, interpretation of the other integer and fractional peaks was an output of WP4.

QUB – Paul Dawson

Many CNT coated glass samples were provided by Toughglass and the Engineering department at QUB. The coating is applied to the glass by spraying a mix of MWCNT + PVP + NaDDBS (sodium dodecyl-benzene sulphonate). After characterising many non-conductive samples, it was decided that we would only look at samples that were conductive. Unfortunately, we were only provided with one sample that had the capacity to carry an electric current. Resistance measurements were carried out on this sample, by the 4-point probe method, gave a resistance value of 0.55 MΩ. The glass surface of this sample was completely black and opaque (transmittance < 10% UV-Vis-NIR region). The coating was also not resistant to abrasion and would simply wipe off during handling. The samples were also analysed by AFM, but we were unable to determine if there was a contacting network of carbon nanotubes on the glass surface due to the overall roughness of the film.

Sharp (10-20 nm diameter) W and Ni precursor tips produced are produced by a lamellar etch technique at QUB (D3.8) and have been used as growth points for carbon nanotubes at Cambridge University (partner 9), the aim being to produce a single nanotube at the end of the metallic tip for use in a scanning tunnelling microscope (STM). This goal has been achieved, with controlled growth of MWCNT's at the apex of these etched tips. An extremely sharp tip pre-cursor ensures that a single MWCNT grows from the tip apex. These tips have been successfully used in STM scans (D6.1), showing faithful replication of a square grating profile that surpasses those obtained with very sharp metallic tips (without MWNT) and mechanically cut metal tips. However, tip damage is prevalent which appears to trace to poor electrical connectivity across the metal tip to MWNT boundary, possibly due to the presence of a thin oxide layer on the W tip precursor structure. Direct growth onto Ni tips has also been achieved. This removes the need to over-coat the W tips with a layer of ITO followed by the Ni catalyst, thus reducing the number of process steps. These tips have also been successfully used for STM imaging of polycrystalline Au and HOPG surfaces. Atomic resolution is achieved on the HOPG surface. Further work is needed on the growth of CNT's from Ni tips in order to pinpoint the ideal growth conditions.

Figure 1 Examples of MWCNT tips grown on (a) W precursor and (b) Ni precursor

Further to deployment of MWCNT tips for STM imaging, the tips were coated with a layer of Au (~ 25 nm) by thermal evaporation, and used in Light Emission STM (LESTM) experiments (D6.2). The tips are rotated during evaporation to ensure an even coating around the CNT. This coating also alleviates the problems with the conduction path for the W tip precursors. The goal was to achieve an enhancement of the light output from the STM tunnel junction due to the MWCNT behaving as an optical antenna. This would therefore improve the quality of photon maps and spectra from metal surfaces and molecular species adsorbed onto these surfaces. Indeed an order of magnitude enhancement of the signal was achieved, compared to standard electrochemically etched Au tips, Figure 2. This enhancement is sufficient to allow the user to spectrally map surfaces in reduced times

and with lower tunnel currents. This will reduce the damage that can be done to sensitive molecules during the spectral acquisition process.

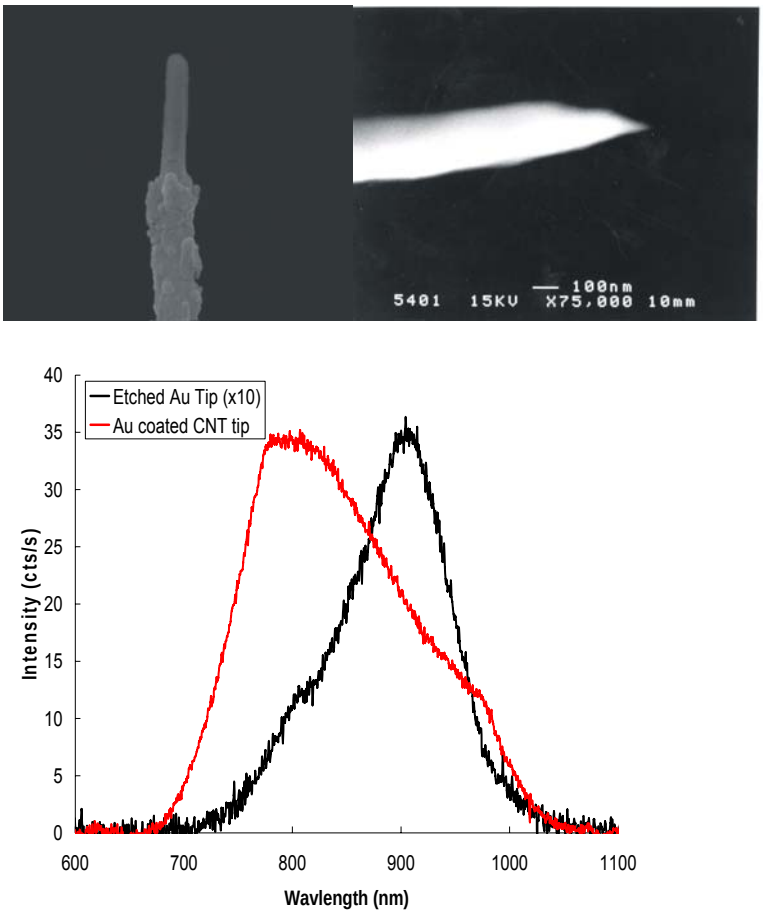
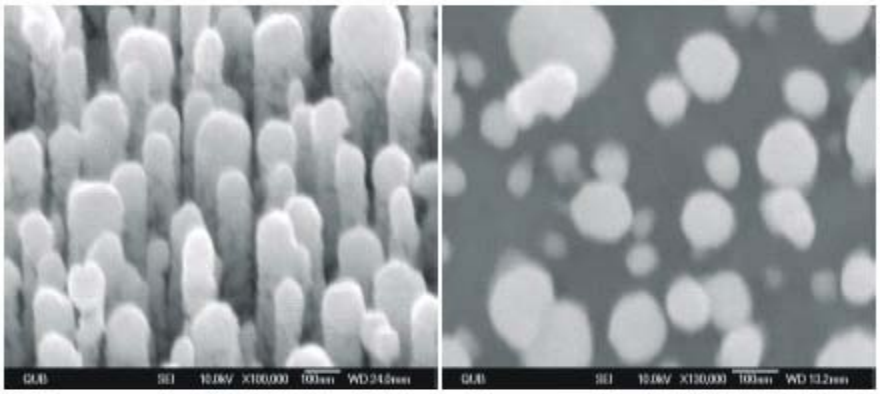


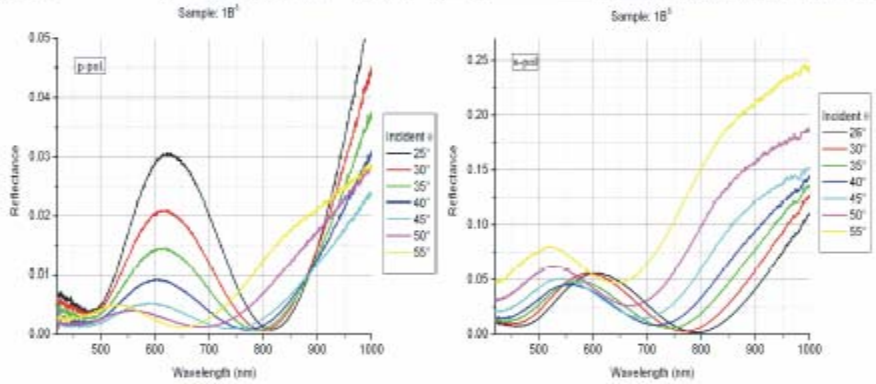
Figure 2 LE-STM spectra acquired using the Au coated CNT tip of (a) along with a typical spectrum from a standard electrochemically etched Au tip, (b). The spectrum from the standard Au tip has been scaled up for clarity. CNT length 380 nm.

Additional investigation is necessary using CNT tips of various lengths prior to publication. This will help us to identify the optimum length for the CNT to give the maximum enhancement and to further understand the enhancement process.

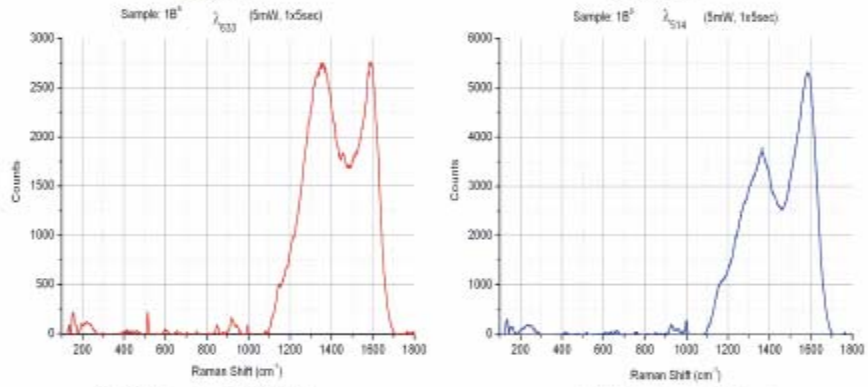
Much effort was devoted to the study of vertically aligned MWCNT's grown on Si substrates at Cambridge University. Tubes of various lengths ranging from 200 nm – 2 µm were supplied to us. The main focus was to characterise these substrates both optically and by Raman spectroscopy (D4.1), with the ultimate goal of obtaining a tuneable substrate for Surface Enhanced Raman Spectroscopy (SERS), (D4.2). Optically, the samples were characterised by measuring the specular reflection of each sample at varying angles and polarisation states. It became apparent, both visually and from the spectra, that these samples were indeed optically active. Samples with CNT lengths in the range 400 – 700 nm displayed a colouration ranging from blue to green to red with increasing tube length. The spectra revealed the nature of this colouration with a peak in reflectance with centre wavelength, λ_p, corresponding to CNT length, L ~ 0.9 λ_p. The spectra where also examined with the white light source polarised in the s and p-states. For the p-polarised source, the intensity of the reflectance peak reduces with angle of incidence, with only a small blue shift at high angles.



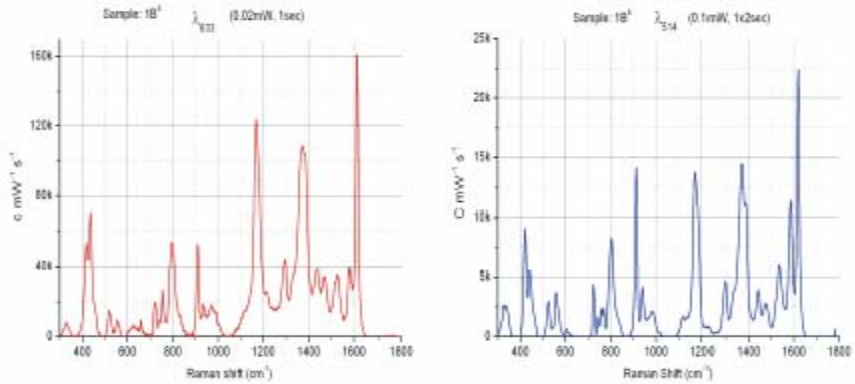
A. SEM images of Ag-coated MWNTs. **Left**, sample tilted 45°. **Right**, top view of the sample.



B. Optical characterisation for p-pol. (**left**) and s-pol. (**right**) at different angles.



C. SERS of Ag-coated MWNTs for excitation wavelength of 633 nm, $5mW$, $1 \times 5sec$ (**left**) and 514 nm, $5mW$ $1 \times 5sec$ (**right**).



D. SERS of crystal violet for excitation wavelength of 633 nm, $0.02mW$, $1sec$ (**left**) and 514 nm, $0.1mW$, $1 \times 2sec$ (**right**).

Conversely, for s-polarisation, the peak blue shifts with increasing angle. We have developed a simple model to describe this shifting, based on thin film interference. The modelling of the p-polarised state is more complex and requires further theoretical input.

The CNT forests were dressed with Ag by either capping, evaporating at normal incidence, or coating, rotating the sample at an incline of 15° during evaporation, Figure 3 A. A number of observations are

made after the CNT's have Ag attached. Firstly, the specularly reflected peak exhibits a red shift for both s and p-polarisations, Figure 3 B. The magnitude of this shift is dependent on the thickness of the coating. The D and G band signals in the Raman spectra are enhanced by a factor of 5 – 10 compared to the bare nanotubes. This is surprising, as the Si peaks from the sample substrates are quenched by the addition of the Ag layer (Figure 3 C – Si peak at 520 cm^{-1} is quenched). Crystal Violet (CV) was used as the test molecule to evaluate the validity of these CNT samples as substrates for SERS. The criteria for a good SERS substrate are that the signal should be enhanced by several orders of magnitude and that the signal should be uniform across the sample surface (i.e. no hotspots). These Ag coated and capped MWCNT forests certainly fulfil the criteria. Enhancements of the order of 10^9 are observed and the intensity is uniform across the Ag region, Figure 3 D. By the appropriate selection of CNT length, the signal enhancement can be tuned to a particular laser wavelength by ensuring that the reflectance peak resides at that wavelength. A number of joint publications with UCAM-DENG are currently being prepared.

QUB – Tony McNally

In WP5 composites of PMMA, polystyrene, polyethylene and a styrene block copolymer with up to 10wt. % multiwalled carbon nanotubes were prepared by melt mixing using a twin-screw extruder. The extent of the dispersion of the carbon nanotubes in the different polymer matrices and their interaction was investigated using a combination of SEM, HRTEM, XRD and Raman spectroscopy. The melt blending of CNTs in molten polymers was readily achieved using conventional polymer processing techniques. The key goal for all composites prepared was to attain uniform dispersion of the CNT in the polymer matrix and avoid aggregation of the CNTs into bundles. This proved to be the very difficult to achieve. Further understanding of the forces (shear and extensional) required to uniformly disperse CNTs in molten polymers will be required. This was partly addressed by performing melt mixing experiments and injecting super critical CO2 into the polymer melt to reduce melt viscosity and alter the solubility of the CNT in the polymer and by functionalising CNTs so as to enhance wetting with the polymer.

Solutions of MWCNTs in water with different surfactants, NaDDBS and poly(vinyl pyrrolidine) were prepared and a method for spraying these solutions onto glass substrates developed, initially at QUB, followed by trials at Toughglass Ltd. The concentration of MWCNTs was varied and these solutions were shown to be stable for up to 14 weeks. It was possible to produce uniform coatings, although not consistently, of these solutions on toughened glass. Solutions having lower concentrations of MWCNTs sprayed onto glass had greater than the 80% transparency required by industrial standards but were not electrically conducting. Conversely, solutions having high concentrations of MWCNTs were not transparent, but were conductive, approximately 8.77 x 102 S/cm, in the best case. The key to successful exploitation of this technology is achieving uniform coatings.

The electrical resistivity, mechanical and barrier properties of the nanocomposites prepared were measured. The lowest electrical percolation was obtained for MWCNTs prepared using an arc-discharge method. MWCNTs prepared using CVD gave a higher percolation. MWCNTs functionalised with carboxyl groups were well dispersed in PMMA, but the addition of –COOH rendered the CNTs non-conductive. For polystyrene MWCNT composites, the effect of screw speed (mixing time) on the composite morphology was examined. An intermediate screw speed of approx. 100rpm gave the composites with the lowest electrical percolation. The high melt viscosity of polyethylene can hinder the dispersion of MWCNTs, thus the melt viscosity of PE and solubility of MWCNTs was modified

during processing by injecting super-critical CO2 into the melt. Also, the effect of using single versus twin screw compounding on structural evolution of the composite was investigated. Composite preparation using a single screw extruder gave a lower electrical percolation than those composites made using a twin screw extruder. Injection of ScCO2 to the PE melt had little effect on the percolation level, but the ultimate increase in conductivity improved by a further 2 orders of magnitude. Additionally, the rheological percolation for the nanocomposites was determined using parallel plate rheology and data used to help interoperate whether a network of CNTs had formed in the various polymer matrices. No improvement in barrier performance to O2, CO2 or H2O was achieved on addition of MWCNTs to the polymers. Limited mechanical testing of these composites was performed as the study extended to focus on the factors that control CNT dispersion.

The aim of this work in task 6.8 was to develop diagnostic/quality control hardware and software, suitable for industrial process control of an on-line coating application. For a CNT coating on glass the diagnostic tool should determine if carbon nanotubes were present on the final product and how uniform the coating was. Raman spectroscopy was used to monitor CNT coatings on glass substrates. In contrast to conventional Raman spectrometers, a fibre optic cable was used to record Raman spectra remotely from the instrument, i.e. for use on a production line. CNTs have unique Raman scattering bands and signature, the intensity and position of these bands change as a function of CNT thickness/coating on a substrate. This was demonstrated in the laboratory, with the characteristic D and G bands of CNTs being non-descript in non-uniform coatings, but clearly discernable in more uniform coatings. Discussions were held with a manufacturer of Raman Spectrometers – Avalon Instruments (now part of Perkin-Elmer) and the feasibility of using a Raman spectrometer coupled with fibre optic cables in a manufacturing environment was confirmed, e.g. Toughglass Ltd. The positioning of the probe during the coating process, before or after heat treatment would need to be determined. Coatings of known thickness and thus D and G band intensities could be used to set upper and lower limits, allowing a degree of quality control – i.e. online monitoring.

Fraunhofer

The Fraunhofer society, represented by the two Institutes IGB (Fraunhofer Institut für Grenzflächen- und Bioverfahrenstechnik) and TEG (Fraunhofer Technologie Entwicklungsgruppe) were involved in the Workpackages 3, 4, 5 and 6.

In task 3.2 Fraunhofer worked on the plasma functionalisation of carbon nanotube in the form of bucky papers and aligned CNTs. Two set-ups for the plasma treatment were built. In the first, a horizontal tube reactor was used and the influence of the treatment conditions like power, duration, flux, and monomer gas composition were assessed. The results were used to develop a parallel plate reactor which is distinguished by a more homogeneous treatment. This reactor was used for the plasma modification of the produced bucky paper as well as the aligned grown CNTs. With regard to the bucky paper treatment, a strong hydrophilisation leading to an instant wetting could be achieved by applying oxygen containing monomer gases. This is necessary for good electrolyte penetration during the actuation measurements, carried out in WP 5. The assessment of the oxygen increase was done by using ESCA. A summary of some the major results of this task can be seen in the following table.

	SWNT			MWNT		
	C	O	N	C	O	N
	Elemental Composition (atom%)					
untreated	94,4	5,1	0,5	97,5	2,5	-
O2 10 sec	82,5	16,7	0,8	93,2	6,8	-
O2 10 min	74,2	**25,4**	0,4	86,8	**13,2**	-
N2 10 sec	92,1	7,4	0,5	96,3	3,4	0,3
N2 10 min	83,8	**15,7**	1,5	84,5	**13,2**	2,5
N2/O2 10 sec	84,7	15,0	0,3	92,2	7,8	-
N2/O2 10 min	76,1	**22,7**	0,4	87,6	**12,4**	-

Table: Elemental composition of plasma treated SWNT and MWNT bucky papers assessed with electron spectroscopy for chemical analysis (ESCA)

Also, a superhydrophobic finishing to the bucky papers could be achieved by applying a carbofluorine monomer gas within the plasma process. This resulted in a water droplet hitting and bouncing over the surface without wetting.

For aligned CNTs, an extensive range of treatment parameters, such as monomer gas composition, power, duration, gas flux and pressure, were assessed. A strong alteration of the CNT shape could be obtained but unluckily an opening of the CNT caps without a strong alteration of the shape was not successful. The following figure shows one representative picture of aligned CNTs after an O2/H2 plasma treatment for 10 sec or 10 min, respectively.

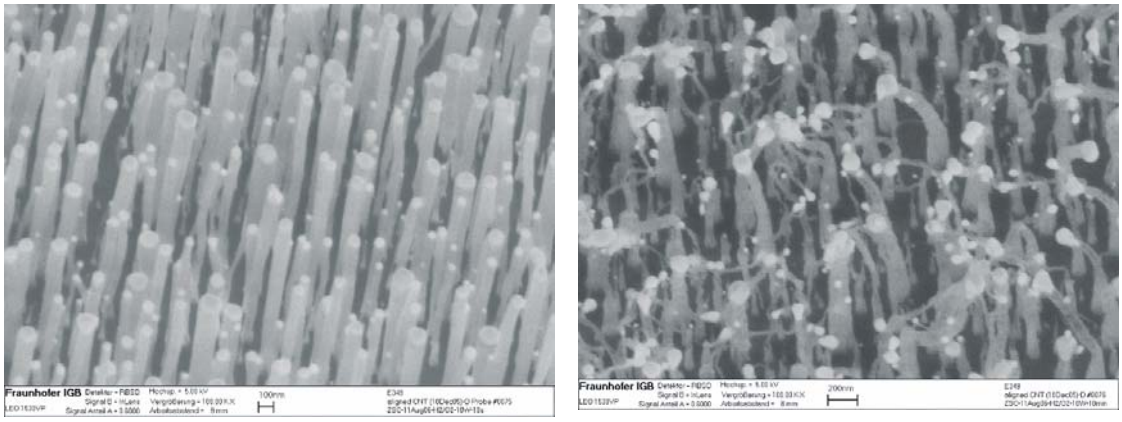


Figure: SEM-pictures of 10 sec and 10 min treatment with oxygen/hydrogen plasma

In task 3.6 Fraunhofer concentrated on the optimized production of CNT bucky papers. The process for the production of bucky papers was successfully optimized. Several parameters have to be accounted for. The surfactant used (SDS, Triton X, etc.); the kind and duration of ultrasonic treatment (bath or tip), the centrifugation, the filter membrane used and filtration technique (vacuum or high pressure) were assessed with respect to the production of a stable bucky paper which could be used for the actuation measurements. In the following figure a brittle (left) bucky paper, produced under non optimized parameters and a stable bucky paper (right) are shown.

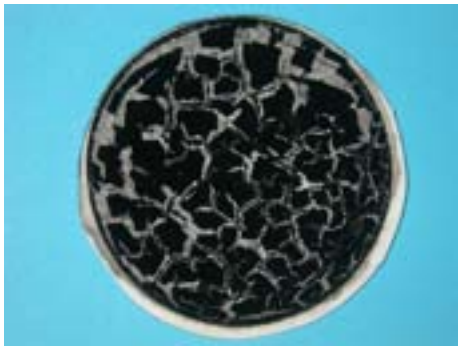


Figure: wrong parameter set

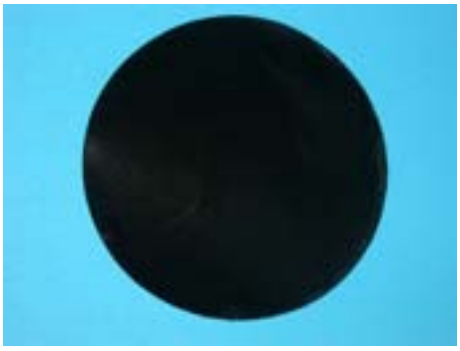


Figure: optimized parameter set

In task 4.1 nanotubes and CNT arrays were characterised. Within the project several raw materials provided by Trinity College Dublin, University of Ulster, University College Cork as well as aligned CNTs grown by University of Cambridge were analysed by SEM/EDX as well as ESCA analysis. ESCA results were manly also used for the characterisation of the material after plasma functionalisation to assess and optimise the production parameters. The analytical results were mainly used to optimize the production parameters.

Fraunhofer worked on the wetting of bucky papers and interaction with electrolytes in task 5.1. It could be shown that the plasma treatment with oxygen containing monomer gases leads to an instant wetting of the bucky papers and therefore systems with a contact angle below 10°. For the actuation measurements, several electrolytes were assessed with variation in their chemical composition, size and valency of the ions and concentration. Sodiumsulfate was assessed as appropriate electrolyte. The advantage of non aqueous electrolytes is the higher potential that can be applied compared to aqueous systems.

A measurement set-up for electromechanical analysing of bucky papers was developed in task 5.2 by Fraunhofer. In the first stage of the task, a test-set-up was built and the actuation performance of bucky papers was analysed. In the following stages, the set-up and the actuators were optimized. As a result, potentiodynamic and galvanodynamic measurements are possible. Increased precision of measurements were achieved by employing an optical sensor (resolution of 3-10 nm), a reference electrode, a shock absorbing system and the control of surrounding conditions. Additionally the measurement set-up is suitable for performing investigations under application of load.
This optimized measurement set-up is shown in the figure below.

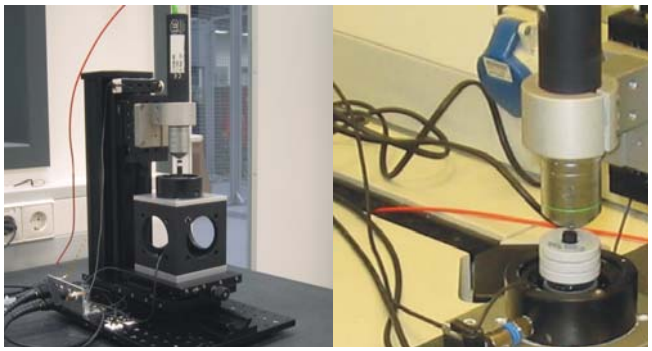


Figure: Measurement set-up for electromechanical analysis of carbon nanotube actuators

In task 5.3, Fraunhofer dealt with investigations on carbon nanotube actuators performance, prepared from varying materials. The best actuation was shown by the bucky papers having a forest of aligned nanotubes grown on their surface. However, those samples have the disadvantage of low mechanical stability. Samples produced from SWNT and purified MWNT give the next best results and are of higher stability.

In terms of operating parameters, it has been proven that displacement of carbon nanotube sheets is proportional with the input potential. Moreover, pre-treatment of bucky papers is recommended in order to achieve higher precision of the measurement and quality of results.

The most suitable electrolyte for carbon nanotube actuators were selected in task 6.4, and investigations on the influence of the pre–load applied on the bucky paper during operation were carried out. As a result, a water based solution of Na_2SO_4 turned out to be the most suitable electrolyte as the actuation of bucky papers was the highest in this medium. Furthermore, in this system the highest actuation was obtained under application of the highest pre-load.
Investigations on the influence of the pre-load on the performance of samples have shown that, for all the systems, the highest actuation values are obtain within the lower range of pre-load (4 - 20 g). Above this weight, in most cases, a sudden drop in displacement can be observed; however, application of the further weight, up to 125 g, seems not to have a significant influence on the performance of the actuators. Furthermore, a new bucky paper obtained from the dispersion of carbon nanotubes in NMP and a bucky papers based on carbon nanotubes grown on the stainless steel plates were investigated and both types revealed the potential for use as actuators. However, more tests are necessary to make a clear statement about their performance.

UCAM-DENG'

The main activity of UCAM-DENG in DESYGN-IT is the production of both MWCNT and SWCNT material for its partners in the forms of films and as controlled arrays structures. With further development of our CVD growth system, substrate sizes of 2" can now be deposited for both MWCNT and SWCNT using a larger stage area as reported in deliverable 3.5. This was made possible by developing and characterising the growth material using a 2" stage (Figure 1).

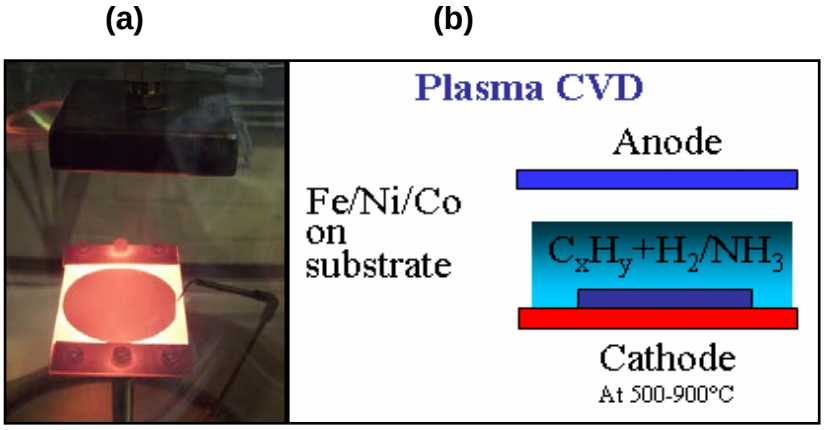


Figure 1 (a) Actual image of the CVD deposition setup along with its (b) schematic diagram.

The formation of CNT films on substrates have many applications but the ability to exploit these films by controlled patterning into array dot structures present itself with even greater applications such as in creating nanoscale device electronics, sensors and micromechanical devices. Films and arrays of both MWCNT and SWCNT are shown clearly in figure 2.

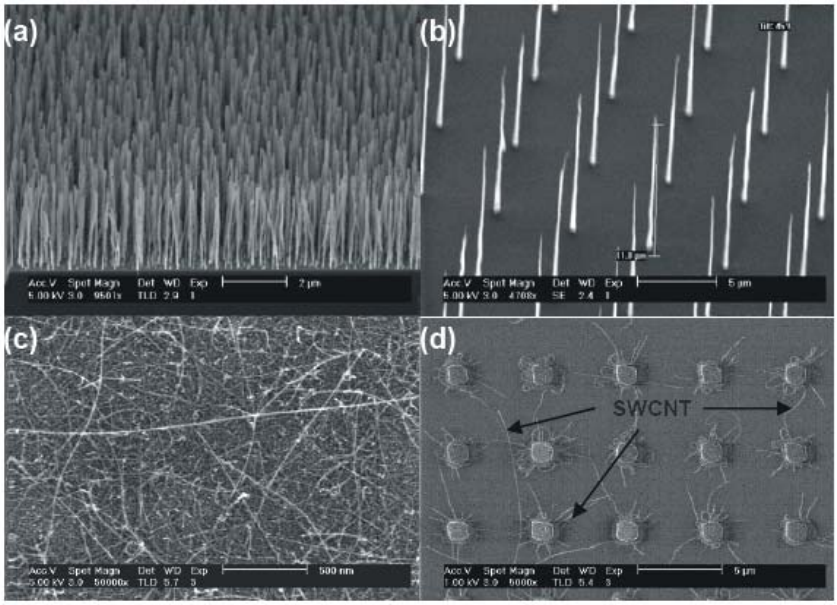


Figure 2 Micrograph images showing (a) a forest of aligned MWCNT and by employing patterned dots (b) array of individual MWCNT is produced. Similarly, by patterning dot arrays, (c) SWCNT film density can be controlled further to produce almost (d) individual isolated SWCNT.

In addition to the efforts to scale CNT production, as was achieved by scaling the CVD deposition method, the initial array structures which were made with electron beam lithography can now be achieved with imprinting. With recent development based on the imprint method, large arrays can be made at a fraction of the time on large wafers and using much simpler systems as compared to electron beam lithography. This is an important factor to make CNT production more cost effective but still able to produce the desired results. Coupled with the CVD's capability to deposit 2" wafers, a commercially viable process is possible.

For MWCNT work, 2" wafer depositions showed good uniformity across the wafer and alongside this development, imprinting had also shown to be feasible, with MWCNT arrays grown similar to those produced with electron beam lithography. Optimisation however is required to improve the separation of the imprint master and substrate at the end of the imprint process. This could be facilitated by improving the adhesion of the patterned polymer to the substrate surface or by increasing the hydrophobicity of the imprint master to create a better anti-sticking surface.

Apart from the efforts to grow MWCNT on large silicon substrates, MWCNTs have been also grown on several different substrate materials that include glass, bucky paper and metal as required by other tasks in the project. MWCNTs were also deposited on metal electrodes on Si substrates (with a thin top insulating layer). This is to facilitate the addressing of individual electrodes for chosen applications. Field emission characteristics from these structures showed low turn on electric fields and good current carrying capacity.

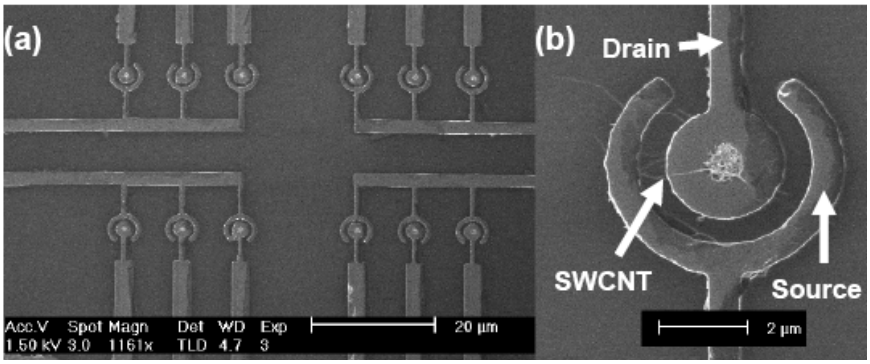


Figure 3 Configuration for an (a) array of SWCNT transistors with a single device shown in (b) showing multiple SWCNT from a catalyst island in contacted by source drain contacts

Using the same CVD system, a rapid thermal method for producing SWCNTs was also achieved for depositions on 2" wafers. This facilitates the fabrication of large scale SWCNT transistor circuits at a low thermal budget. Using catalyst islands, the density of SWCNT originating from each catalyst island can be controlled. In addition, it was also found that the SWCNT from these catalyst islands had formed as individual isolated structures making them ideal for SWCNT analysis. The rapid thermal method produces SWCNTs that is free of amorphous carbon on its structure and of its surroundings, a criterion which is important for device fabrication. However, further work is required as the SWCNTs produced had varying electrical characteristics, with both metallic and semiconducting SWCNTs having formed in equal numbers. This is directly related to the physical variations of the SWCNTs as measured by Raman, TEM and AFM. As bottom gate characteristics were only measured for the semiconducting SWCNTs, the best sub threshold slopes were 340mV/dec. This can be improved with the use of localised gating and thinner gate dielectrics. However, good characteristics were observed from these measured structures such as a high maximum saturated

current, IDS, max of 12µA and on/off ratios of 104 to 105. These transistors were typically made by mapping contacts onto individual SWCNT originating from the catalyst dots. In order to circumvent the need for mapping, radial contacts (figure 3) were explored as these contacts increases the success for connecting the SWCNTs originating from each catalyst island. The transistor characteristic of such a measured device is shown in figure 4b and is compared with an individually contacted SWCNT. For the measured radial contact device, improvement in current capacity was marginal and due to the contact made to several SWCNT, the on/off characteristics were poorer at higher VDS. The importance here however is that a regular wafer scale process could be developed for integrated circuits based on SWCNT transistors using this type of radial contacts.

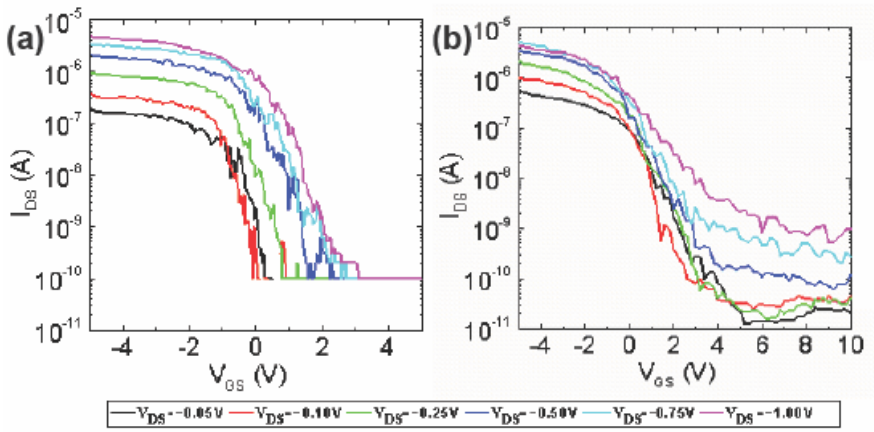


Figure 4 Gate transfer characteristics of semiconducting SWCNT as shown for (a) individually contacted SWCNT and (b) radial contacts made to several SWCNT.

Apart from the growth on substrates, MWCNTs were also grown directly onto metal tips. In the initial work, individual MWCNTs were grown on tungsten (W) tips covered with the catalyst material (figure 5a). This facilitated early research into the use of these tips as AFM and STM probes. With the STM probes, however it was found that the conductivity between the MWCNT and W tip was not good enough. In order to improve on this, MWCNTs directly grown from nickel (Ni) tips were investigated (figure 5b). Results showed that MWCNTs can be produced on these tips but reproducibility to form a single MWCNT per tip was usually rare. The achievement of these tips have showed practical application and these structures could even be developed further into other applications such as sensors and emission tips.

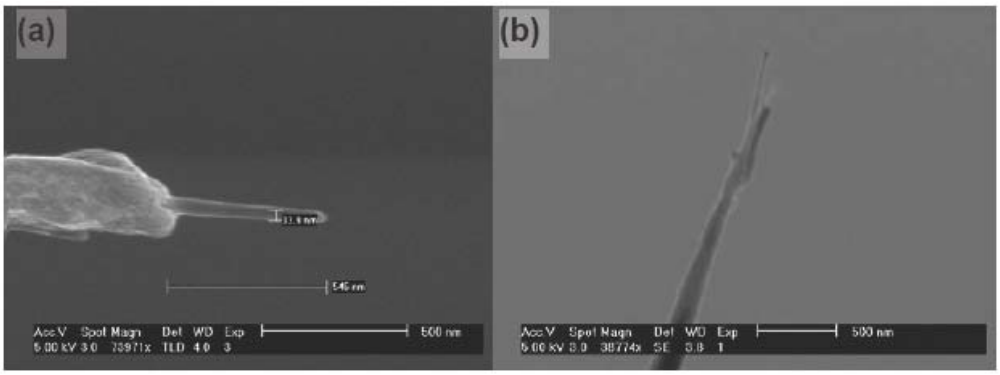


Figure 5 MWCNTs grown (a) on W tip deposited with ITO/Ni as the catalyst material (b) directly from a Ni tip

TG

Potential commercial opportunity exists in the retail refrigerated sector and the bus and coach market as currently products made by glass makers are used. If an on line, process can be developed and used by a processor substantial supply chain benefits would be available. The requirements have been defined in the Book of specifications.

TG, working closely with QUB, focused on the testing of formulations of CNT coatings to establish conductivity with no less than 80% light transmission.

It was agreed that QUB should take the lead in terms of material supply and lab demonstration with TG providing the resource to apply the material in terms of labour and equipment.

ST & D Ltd

Sensor Technology Devices is a spin-out of the University of Ulster and therefore has close relationship with the NIBEC (UU) particularly in the areas of sensors and nanotechnology. The focus of the Desygn IT project was to develop the use of low-cost nanostructured field emitters into a prototype gas sensor. The work in task 6.5 concentrated on 2 main areas: Growth of vertically aligned CNT electrodes for low turn on voltage DC plasmas and ZnO nanoneedles as an electrode

Study 1 Growth of vertically aligned CNT electrodes for low turn on voltage DC plasmas.

Carbon Nanotube (CNT) based electrodes have superior field emission properties to metal electrodes produced by conventional methods. CNT induced plasmas have been shown to operate at ~22 % less voltage while increasing the radiative output by ~10%. They are capable of delivering high discharge currents which offer an advantage of detection of trace level of gases such as NO which cannot be easily detected by other means.

Si(100) substrates sputtered with Co catalyst layer of thickness 0.5, 1 and 3nm were used for the growth of vertically aligned multi walled CNTs (MWCNTs) by Microwave Plasma Enhanced Chemical Vapour Deposition (MPECVD) (Figures 2 and 3). The substrates were pre-treated with an N_2 plasma at 7000C, 600 W to produce catalyst islands on the surface from which CNT nucleation and growth can start. CH4 was used as the source gas and the growth times were varied from 5-15 minutes.

A purpose built Surface Discharge Test Device Figure 1 is used in a vacuum chamber (base Pressure ~3x10-2 Torr). The electrical circuit as shown in Fig.1 b, is used for the measurements, U is the DC supply voltage. RB is the ballast resistance (variable 0.3–3 MW) and RM is the measurement resistance (10 kW fixed). The cathode is comprised of vertically aligned MWCNTs with diameter 60-80 nm, length ~ 20 mm. The anode is a stainless steel screw with an anode – cathode gap (d) of 200 mm. All the experiments were with working pressures between 1-50 Torr in Argon.

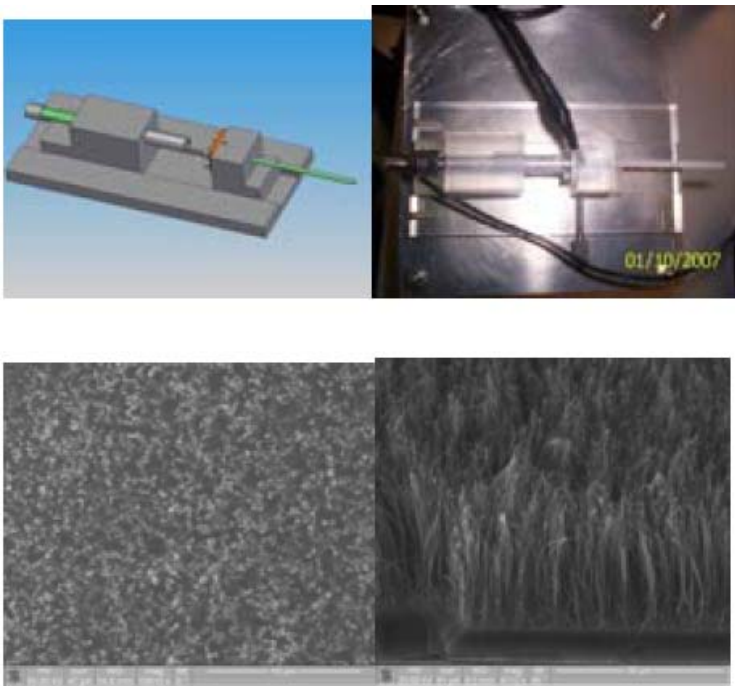


Figure 1: Microdischage device and SEM image of CNTs on Ni catalyst before use.

Even though the IV curves (Figure 4) clearly resemble standard DC discharge characteristics, electron production may be due to the combined effect of field-emission and secondary emission from ion bombardment of the MWCNTs.

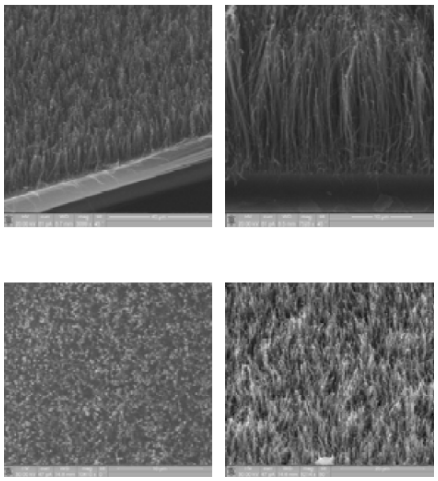


Figure 2: (a) MWCNTs on 1 nm Co/Si, (b) MWCNTs on 3 nm Co/Si after 15 minutes of growth. The

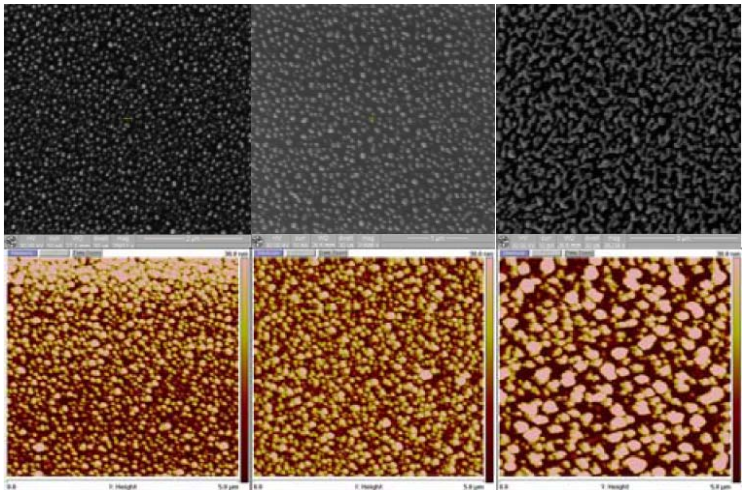


Figure 3: Co islands after N2 pre-treatment on 0.5 nm (a, b);1 nm (c, d); (e, f) 3 nm thick films

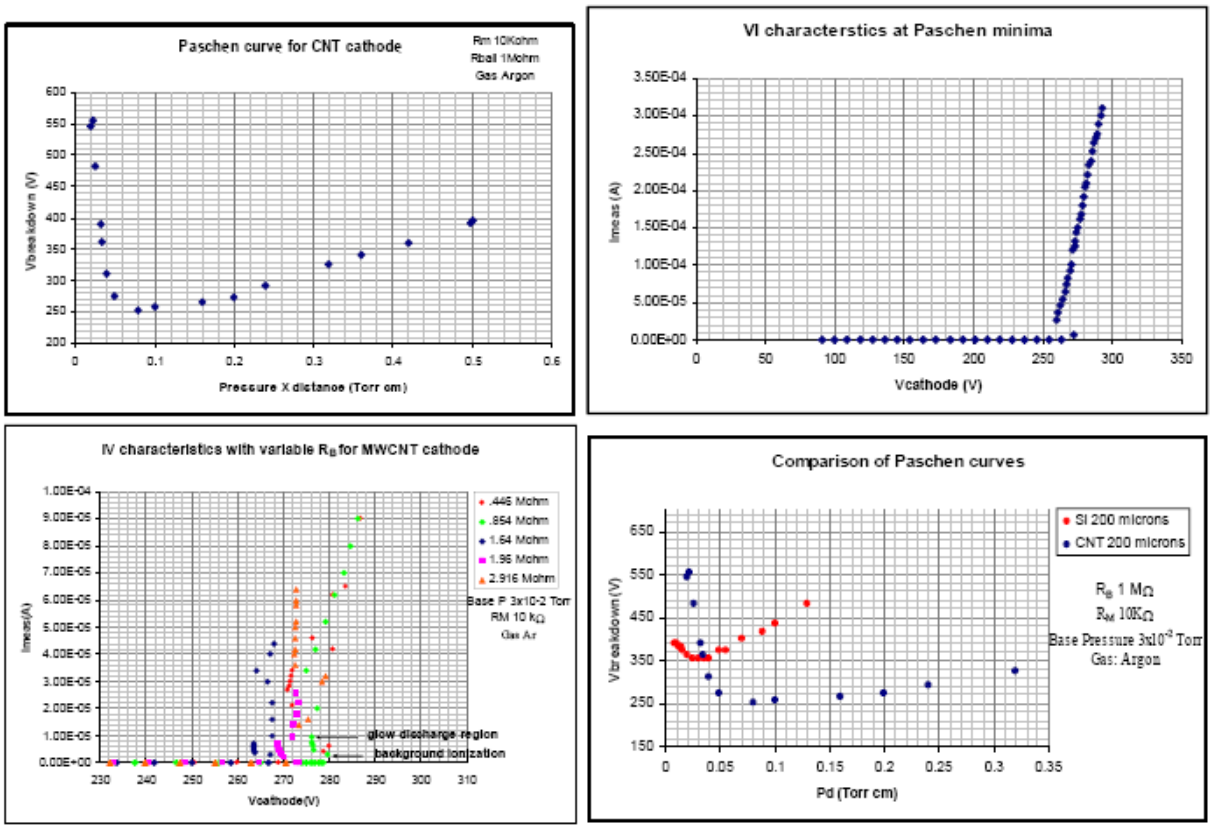


Figure 4: Paschen Curve for CNT cathode; IV characteristics with Ballast changes; Paschen Minima; Comparison of Paschen Curves with and without CNT's

In this study, ***it was shown that with a CNT based electrode one can generate DC low pressure plasma with about 30% less operating voltages and ~ 10^3 times more current.*** Also noted is the effect of controlling ballasting, which affects the CNT damage and the optimum conditions. ***The next step would be to couple up an OES system with the microplasma device and one can look at specific spectral lines coming from different gas species as well as look for the increase in total radiative output, as predicted. We have also proposed a mechanism as to how the plasma could be initiated in the CNT based micro plasma device, with the help of field emission from CNTs.***

Study 2: ZnO nanoneedles as an electrode

One dimensional semiconducting nanomaterial of Zinc Oxide (ZnO) nanowires, nanobelts, nanoneedles etc. have attracted research interest because of their unique physical and chemical properties and potential applications in electronics, optoelectronics, field emission displays, piezo electric devices and sensors. ZnO has a direct band gap of 3.37eV and a room temperature exciton binding energy of 60 meV which makes it an ideal candidate for optoelectronic applications. Growth of ZnO nanostructures by vapour transport and condensation process, using physical vapour deposition technique were studied. To understand and optimise the growth parameters and conditions for the growth of nanostructures, gold (Au) catalyst were prepared using pulsed laser deposition, evaporation and nanosphere lithography for the production of Zone nanostructure. Cobalt (Co) catalysts of various thicknesses were prepared using RF sputtering (Figure 5).

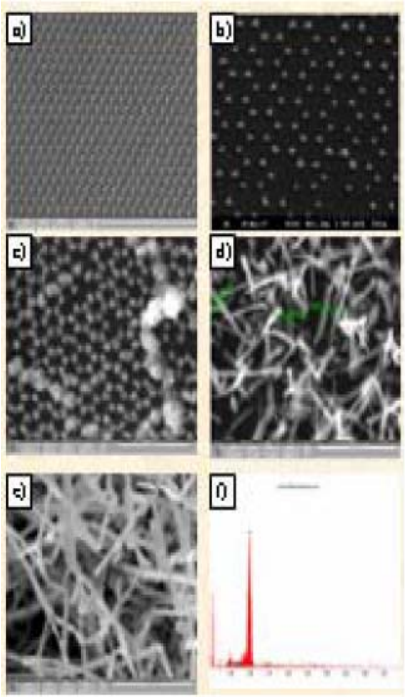


Figure 5: Self assembled Polystyrene nanospheres on Si, b) Gold pattern on Si substrate (c),(d, e) ZnO nanoneedles grown on gold patterned Si(100) substrate at a growth temperature of 9600C. (f) The EDX spectra showing the presence of carbon impurity(from graphite)..

A horizontal tube furnace with an alumina work tube was used for the growth of ZnO nanostructures. The source material was placed at the centre of the tube at 900^0C to 1000 C and the substrates placed at a colder region typically 5 to10 cm away from the source downstream to the carrier gas (Argon) flow. The growth time was varied from 30 minutes to an hour and the furnace was allowed to cool down to room temperature under constant argon flow.

ST&D Ltd has successfully synthesised ZnO nanostructures by physical vapour deposition and identified the suitable deposition conditions for various ZnO nanostructures (Figs. 6 & 7). Surface morphology and growth direction were assessed by SEM respectively. ***EDX results from SEM and XPS revealed the ZnO nanostructure and the presence of carbon and gold catalyst was also identified. The Raman scattering of ZnO nanorods and nano-needles indicated the good crystal quality with nearly defect free structures of ZnO hexagonal wurtzite structure. Measurement of field emission properties, optical properties, gas sensing properties of ZnO nanostructures are currently underway.***

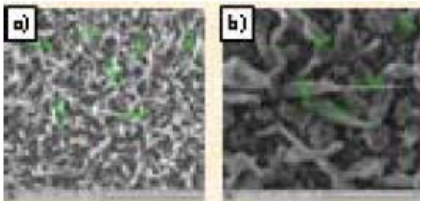


Figure 6: (a), (b) ZnO nanoneedles grown on 20nm Co /Si(100) substrate at a growth temperature of 940oC. The ZnO have a diameter of ~100nm and a length of ~3µm. The nanowires at the tip have a diameter ~30nm.

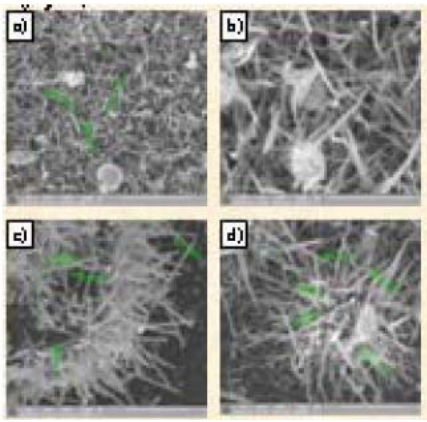
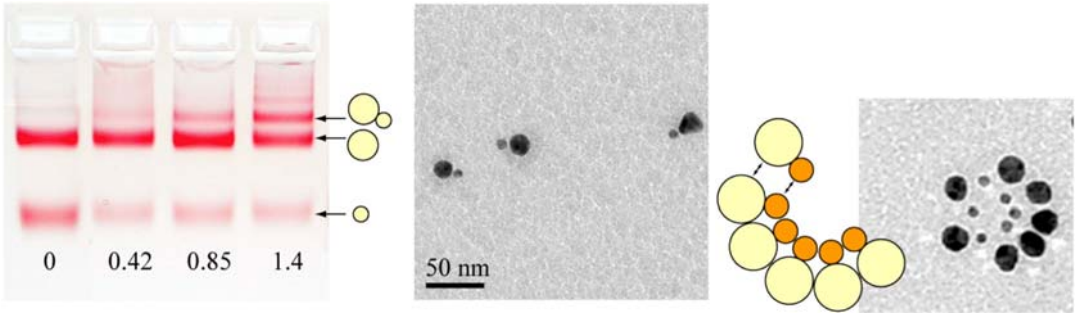


Figure 7 (a) ,(b) ,(c) ,(d) ZnO nanoneedles on 10 nm Co/Si The ZnO nanoneedles have a diameter of ~ 400nm and a length of ~ 7 µm

MSU

The work on programmed self-assembly within task 2.6 has demonstrated some important steps towards the ultimate goal in nanotechnology: the realisation of a bottom-up fabrication technology for complex structures. In a theoretical study, that is published now, some parameters were introduced that could be of importance for the engineering of large and complex studies and that answered questions like “how complex must the building blocks be for this particular structure?”. In an experimental approach (two papers), DNA was used as a smart glue attached to gold nanoparticles and with some novel ideas building blocks were made that in principle could build arbitrary structures. Some results are shown in fig2 below, where gold nanoparticles of two sizes are assembled into dimmers that are then let to assemble into larger rings. In another study we used a long single stranded DNA (7.2 kilobase genome of the virus M13mp18), and by using about 200-250 short synthetic oligonucleotides, the long one was folded into a rectangle with dimensions of about 100*100 nm2. The method is called origami. We then showed how to use the DNA rectangle as a kind of nano-breadboard and made a pattern of proteins with a resolution of 5 nm (one paper). See figure 2 below for details. ***This also suggests a possible route towards large scale integration by self-assembly. By using the origami method for self-assembly at the nanoscale and combine this with top-down methods we might have a realistic way towards this goal.***



a) **b)** **c)**

Figure 1. a) Separation of dimers using electrophoresis. **b)** TEM images of the dimmers.. **c)** Dimmers that are further let to self-assemble into larger formations in a second step.

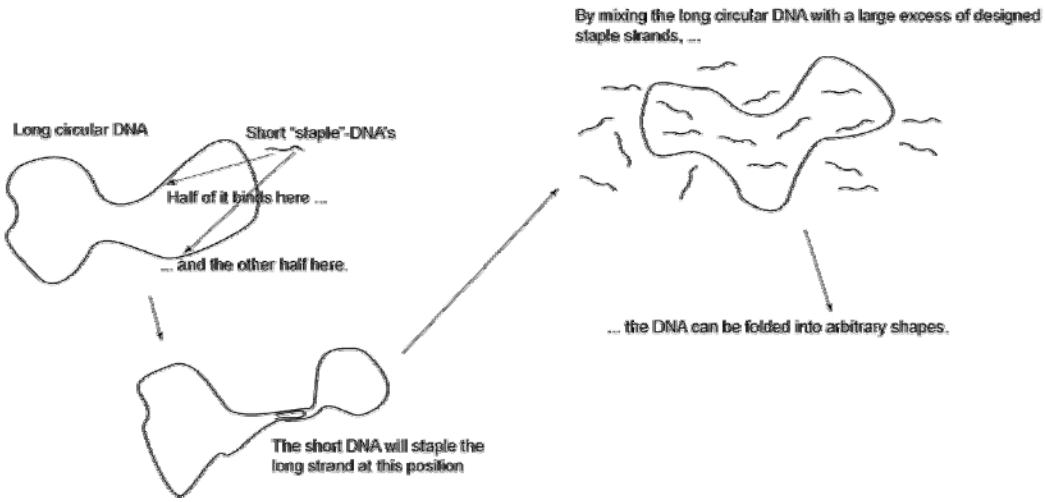


Figure 2. The principle of the DNA origami method. The single stranded DNA scaffold of 7 kilobases is folded by the help of approximately 200 “staple” strands. Arbitrary shapes can be created.

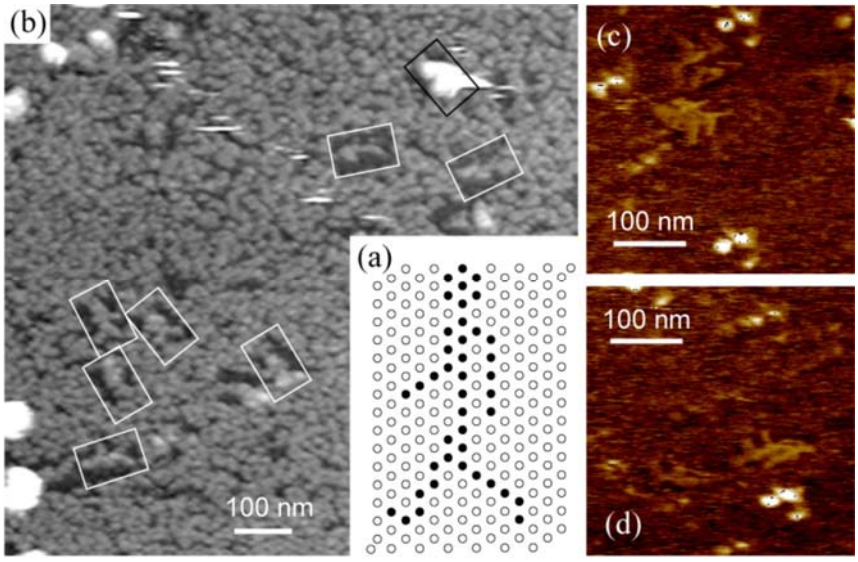


Figure 3. AFM images of a demonstration of the DNA breadboard origami method. A pattern of a walking man is defined into the origami breadboard according to the principle shown in fig MSU.2. Here biotin ended protruding sticky ends are combined with the protein streptavidin that are the nanoparticles in this case.

The tasks 4.5 on field emission properties of carbon nanotubes and 4.6 on electromigration of iron inside carbon nanotubes were both completed successfully (see the reports D4.5.1. and D4.6.1). Field emission is reported by UL. In the study on electromigration iron containing carbon nanotubes was used and showed an onset of motion due to the electron. In-situ TEM probing was used experimentally. ***A critical current density of 7 10^6 Acm^{-2} was found for tubes with a diameter of 20-80 nm*** (fig.4). ***The resistance of the CNTs was several kΩ and scaled as the inverse radius squared, indicating that the electron transport was diffusive. Furthermore, carbon nanotubes were also used as kind of pipette, using the electromigration for transporting the iron in and out from the CNT (one paper published)***.

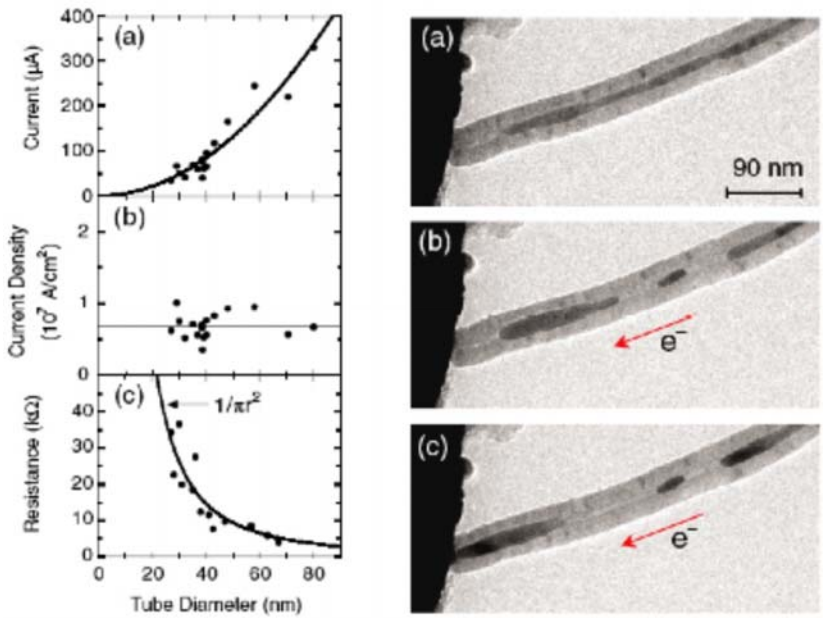


Figure 4. Electromigration of iron inside a carbon nanotube. The onset of electromigration is about 7 10^6 Acm^{-2}.

The part on task 6.3 that concerns the demonstration of a nanoelectromechanical device is reported below by partner UL. During MSU's work on this task, using in-situ TEM probing, ***an unexpected phenomenon was discovered – at high enough current the conductivity suddenly increased by several orders.*** Large electric currents in nanowires can easily cause the motion of atoms, which decreases their current-carrying ability and is a major cause for failure in nanoscale electronic circuits. A new and different effect was observed in MSU's experiments, in which a large current passing through thin molecular nanowire bundles of $Mo_6S_{9-x}I_x$ (MoSI) causes the material to self-organize in such a way as to reduce the electrical resistance to the charge carriers. ***Real-time, in-situ transmission electron microscope measurements clearly show current-induced crystallization occurring simultaneously with a gradual increase of the electrical conductivity by up to 5 orders of magnitude, to 10^5 S/m, reaching current densities of > $3*10^6$ A/cm2. The process may enable in-situ crystallization and further optimization of conducting properties in molecular scale MoSI interconnects in molecular electronics circuits. A paper is in preparation on this topic together with partner IJS.***

NTERA:

In Task 6.6 NTERA produced samples of CNT films and CNT electrodes in devices prepared by screen-printing process. The main technical challenge NTERA has encountered in integrating CNTs as super-capacitors into its NCD^{TM} electrochromic display technology have mainly been related to processing and mechanical properties.

In the early stage of the project, CNT films screen-printed and thermally annealed onto ITO glass substrate tend to show very poor adhesion to the substrate, as well as very weak internal cohesion. Ink formulations incorporating adhesion-promoting agents have significantly improved adhesion and mechanical properties of CNT-coated ITO substrates Comparison with previous measurements on pure CNT films have shown similar capacitance and charging kinetics.
Electrochromic devices comprising screen-printed CNTs presented unsuitable morphology at the macro level: The surface roughness of the films was high, due to the presence of what are believed to be CNT bundles, which were “sticking out” of the base film (the target thickness was ca. 15-20 microns) printed on top of conductive glass substrates.

Once these printed substrates are assembled with counter-electrode substrates to form a “sandwich-type” device, the CNT bundles create internal shorts by physically coming in contact with the counter-electrode in the majority of devices. These internal shorts eliminate the bistability of the display (i.e. the display image self-discharges when externally opening the circuit). Bistability confers remarkably low power consumption to NTERA’s technology and is therefore a critical performance criterion. In this context, traditional dispersion methods (ultrasound, three-roll milling) applicable on small ink volumes and alternative formulation components (commercially available organic solvents, binders, and dispersion additives) were used. None of these approaches sufficiently improved the dispersion quality.

CNTs were also incorporated into “monolith type” devices, where the CNT film is the last of a stack of porous layers printed on a transparent and conductive substrate. For this purpose, low temperature formulations were developed showing the same dispersion problems as high temperature formulations for “sandwich type” devices. However, working single icon demonstrator devices with monolithic design were assembled.

Devices of nanostructured materials were then test at both the electrode and the device level in task 6.7.

At the electrode level for the high temperature process, CNT films on conductive glass were overprinted with white reflector material and the electrochemistry was compared with results from single CNT films. Both electrodes show similar electrochemical capacitance, reversibility and kinetics. The electrochemical properties of the double layer electrodes meet the requirements for “sandwich type” displays.
Electrochemistry of CNT films made from low temperature formulations show lower capacitance and kinetics compared to high temperature processed films. However, for both process temperatures, CNT films show always higher capacitances per weight than the traditionally used counter electrode materials (Table 1).

Table 1: Capacitance per gram of different counter electrode materials.

	High temp. process	Low temp. process
ATO	**~3 F/g**	**~2 F/g**
Carbon black	**~10 F/g**	**~5 F/g**
TCD CNT	**~20 F/g**	**~6 F/g**
UCC CNT	**~27 F/g**	**~21 F/g**

At the device level, the issue with internal shorts, mentioned above, leads to a yield of only 40 % of bistable "sandwich type" electrochromic devices. Bistable devices with high temperature processed CNT counter electrodes behave very similarly to devices with ATO counter electrode (charge-discharge and contrast vs. voltage).

Low temperature processed CNT electrodes were incorporated into monolith type displays with performance similar to "monolith type" electrochromic devices comprising traditional counter electrode materials. Exhaustive tests were not performed on those devices, because testing standards for "monolith devices" are currently under development.

Task 6.8 related to production process control and has been downshifted in priority for two different reasons:

1. The challenges encountered in task 6.6 and task 6.7 (development of screen-printable formulations of CNT-based inks convergent with NTERA's NCD^{TM} product manufacturing scheme, while meeting performance criteria – see above).
2. NTERA has recently changed its focus mainly towards flexible "monolith type" architectures. As a consequence, development of "monolith type" devices comprising CNT electrodes is more beneficial in the context of commercialisation compared to the development of online testing methods for "sandwich type" devices.

The basic in-process Quality Control method envisioned for verifying minimum CNT-based film quality, both in terms of film thickness average and roughness, was profilometry. This was verified as an adequate method in the R&D environment with a DekTak stylus profilometer in the course of this project, and it is expected that this method would be transferable in the manufacturing environment without much difficulty.

In Task 7.2 a technico-economic analysis of CNTs in electronic display applications was performed based on the input from the Book of specifications defined in task D7.1. Specifications which have been assessed were:

- General and optical specifications (contrast ratio, power consumption of a device)
- Electrical specifications
- Electrochemical performance (characteristics of a CNT film)
- Safety Regulation
- Cost
- Purity
- Processability

Incompatibilities were found in the processability (impact of the ink quality on yield). Aside from that, CNTs would appear to meet all other requirements for technico-economic viability that have been assessed.

In task 7.4 NTERA carried out an extensive commercial assessment of the use of CNTs in display applications. In the lifetime of the project, prices for commercially available CNTs have dropped dramatically. As a consequence, data generated from single electrode experiments show, that in terms of cost performance CNTs outperform ATO, which is one of our traditionally used counter electrode materials. On the other hand, for “sandwich type” devices, production yields were not acceptable (40 %)

The first trials of CNTs in “monolith type” devices have shown more promising results. This is very positive on one hand, as recently the low cost flexible “monolith type” design became more interesting from a commercial prospective. On the other hand, this development will come along with an even higher pressure on raw materials costs.

UL:

Field emission (FE) properties of tube and bamboo like carbon nanotubes (CNT) possessing single and multi wall structures were investigated (see Figure 1) using a scanning tunnelling microscope compatible with a transmission electron microscope (TEM-STM)..Knowledge of the properties of various forms of carbon nanotubes is invaluable for possible nanotube applications in field emission flat screen displays. These nanotubes had been grown in partner's laboratories. ***Results showed that CNT grown by the novel supercritical fluid method exhibit FE properties comparable to CVD grown nanotubes (results published in Adv. Mater. 19, 3043 (2007))***. ***FE of bamboo-like nanotubes starts at higher local field values in comparison to nanotubes with tube like structure (true for both single and multi-wall nanotubes).*** FE curves for tube like CNT fit with the Fowler-Nordheim equation when work function of 5 eV is used; however, for the bamboo like nanotubes the work function can reach 8 eV. Failure currents and voltages for all types of nanotubes were determined, and ***it was shown that at high voltages bamboo like nanotubes are more stable than tube like nanostructures***. Results were published in AZojono J. Nanotech. Online (2007) DOI 10.2240/azojono0123.

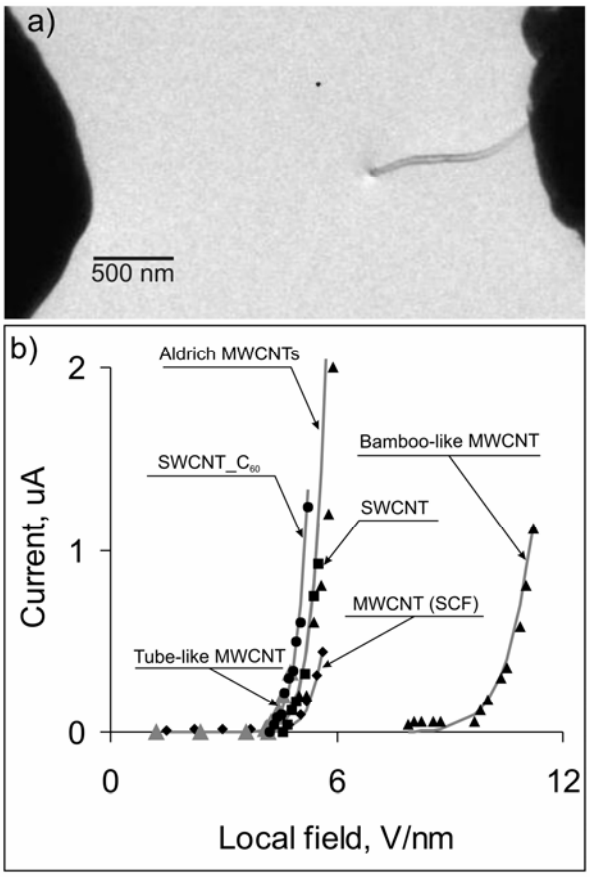


Figure 1: *(a) A TEM image of a CVD grown multiwall carbon nanotube during field emission measurements*
(b) Current dependence on local field for different types of CNT. Solid lines fit with Fowler-Nordheim equation calculated using work function of 8.1 eV for bamboo like nanotubes and 5.1 eV for others.

Conductive properties of differently structured carbon nanotubes grown by the CVD and supercritical fluid methods were investigated and compared (Figure 2). Conductive properties of nanotubes produced by the partners were compared with commercially produced ones (Aldrich). Nanotubes were classified into 2 groups:

1. Nanotubes with high conductivity (CVD grown nanotubes: single-wall, multi-wall and single wall nanotubes filled with C60 molecules);

2. Multiwall nanotubes with low conductivity (SCF grown, bamboo like nanotubes and nanotubes produced commercially by Aldrich).

The low conductivity of commercially produced nanotubes (grown by the CVD method) and nanotubes grown in laboratory by the SCF method is due to nanotubes having amorphous outer layers. The low conductivity of bamboo like nanotubes is explained by the presence of junctions in their structure. Nanotube failure parameters were determined. ***It was shown that bamboo like nanotubes can operate at high voltages, i.e., up to 30 V.*** Results were published in AZojono J. Nanotech. Online (2007) DOI 10.2240/azojono0123.

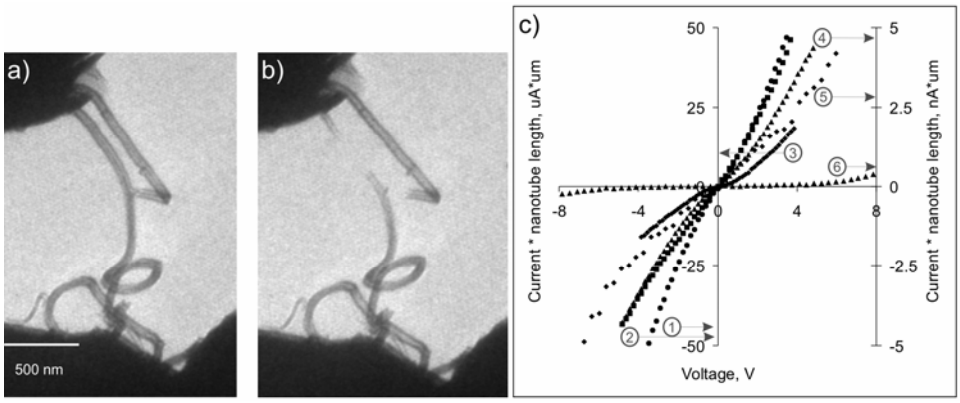


Figure 2: *(a) MWCNT grown by the CVD method, b) Breaking of a nanotube during a two-probe measurement; (c) A comparison of I(V) curves of different types of CN.: 1 -SWCNT filled with C60 molecules, 2 - empty SWCNT, 3 -MWCNT grown on a Co/Mo catalyst, 4 - Aldrich commercially available MWCNT, 5 - MWCNT grown on a Pd/Mo catalyst, 6 -MWCNT grown by the supercritical fluid method.*

Mechanical properties of carbon nanotubes with different diameters were investigated. Instrumentation needed for the investigation of mechanical properties was developed. ***A description of a scanning probe microscope inside a transmission electron microscope was published in a chapter of the book "Fundamentals of Friction and Wear on the Nanoscale" (Springer, 2007).***

A two terminal nanoelectromechanical (NEMS) device based on Mo6 nanowires was demonstrated using the TEM-STM system. Dimensions and mass of active elements in NEMS devices is very small, therefore they work much faster than micron electromechanical devices. These devices have extremely low power consumption and heat capacity. The density of a NEMS device can reach even 1012 devices per cm-2. Figure 3 shows the schematics of the experimental setup and the forces acting within the nanoelectromechanical device.

Two requirements must be fulfilled for the device to operate in an ON regime:

1. Before switching the device ON, it has to be ensured that, the gradient of the van der Waals force is lower than the force constant of the nanowire. This can be achieved by changing the distance between the nanowire and the contact
2. The device will be turned ON only if the sum of electrostatic and van der Waals forces is high enough to make the nanowire jump into the contact.

To achieve an OFF regime, the elastic force of the nanowire has to exceed the adhesion force in the contact when the electrostatic field is reduced.

Figure 4 shows an image sequence of a Mo6 based nanoelectromechanical device during the voltage sweep between the Mo6 nanowire and the gold electrode. A typical I(V) curve of the voltage sweep demonstrates that there is a jump in current during the ON and OFF events at 42 V and 5 V respectively. ***The Mo6 based device is robust and does not exhibit mechanical failure during the ON – OFF event contrary to other ON-OFF devices (based on carbon nanotubes) presented in the literature (Small, 12, 1484-1 (2006))***.
If contact area is reduced and material with lower adhesion is used for the production of the contact, then the device can be switched off at lower electrostatic fields. Therefore, a Mo6 nanowire is used instead of a gold electrode. An article on this is currently under preparation.

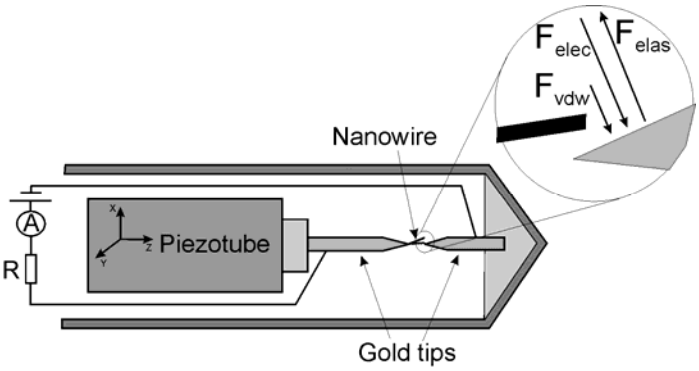


Figure 3*: TEM-SPM experimental setup for in situ investigation of nanoelectromechanical devices and schematics of forces acting within the device.*

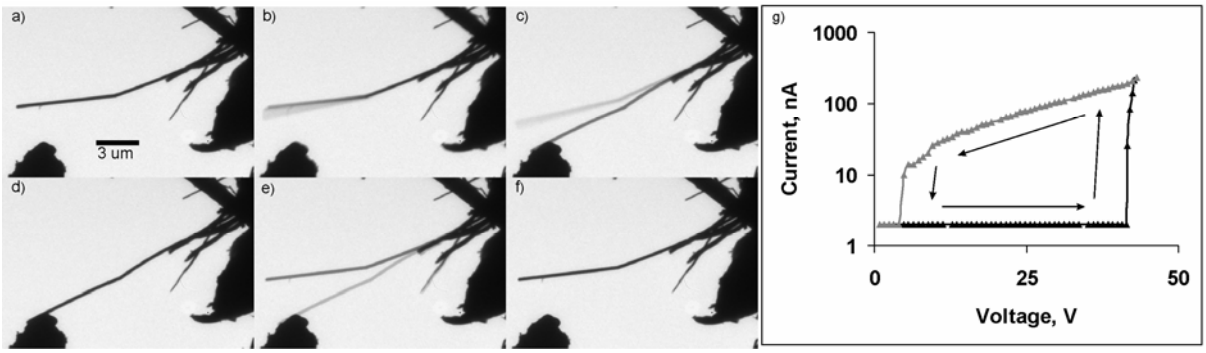


Figure 4: *TEM image sequence illustrating the operation of a Mo6I3S6 nanowire based ON/OFF device. a) The initial position of the nanowire and the counter electrode at zero voltage applied between the electrodes; b) The nanowire moves towards the counter electrode by electrostatic field); c) The nanowire jumps-to-contact; d) The nanowire in contact with the counter electrode; e) The nanowire jumps-off-contact when electrical field is reduced and returns to its initial position; f)* The nanowire after the ON/OFF cycle at zero voltage; g) A typical I-V curve that clearly shows jumps in current during the ON event at 42 V and the OFF event at 5 V.

Problems of the Period and Corrective Actions to be taken:

A problem has arisen in the second part of 2.6. Unfortunately, we have been seriously delayed in the DNA and PNA functionalisation, because the functionalised entities could not be imaged with the AFM. Working with single molecules, they were simply too weakly bound to the surface, so no progress can be made until this is sorted out. The problem is due to surface incompatibility (i.e. different charges) of the different molecular components. An investigation of surface preparations to ensure electrostatic attraction between the analyte and the surface has started. Thus, DNA is different from the MOSI nanowire for example. The goal was to use SiO2 as a substrate because this would ensure that electrical contacts to the circuit were made. Another problem encounter was that the right combination of buffer that allows DNA recombination without resulting in aggregation of the nanowires has yet to be found. These problems unfortunately could not have been anticipated, but it is believed that they are not insurmountable.

The end date for the task 4.6, “Conductivity properties correlated with microstructure of SCF grown CNT and of arc discharge grown CNT” was extended to Month 2. This was to allow more time to characterisation on the increased amount of samples.

5.5 Supply of CNT coatings- With the assistance of budget re-allocation QUB are preparing the CNT coatings and will be present on site when they are applied

6.8 On line process measurement- QUB are developing equipment in the lab to demonstrate this process. An initial report dated 7th November has been tabled

MWCNT for SERS characterization in QUB requires more uniform diameter samples with good density distribution for controlled heights between 250-600nm. UCAM-DENG is currently in progress to achieve these conditions.
Also, MWCNT grown on tungsten tips have not been ideal for the purpose of STM tips due to a poor interface contact which results in a poor conduction between the nanotubes and tungsten. Tungsten tips are to be made in UCAM-DENG to reduce the oxidation of the tungsten tip prior to the catalyst deposition necessary for the MWCNT growth.

Finally, the attempt to achieve separation of metallic and semiconducting nanotubes via macroscopic dielectrophoresis had a negative outcome. This was due to the choice of method. Nevertheless, key lessons emerged from the experience that point toward successful implementation. Scale up of dielectrophoretic separation would be a significant toward implementation of many nanotube applications. Although several high profile publications have speculated about separation of metallic and semiconducting nanotubes, the practical implementation has proven to be extremely difficult, if not impossible. It is not felt that it would not be productive to invest resources at the required level to investigate this issue further since the outcome is not on the critical path of the project.

Dissemination and use the Knowledge

The final Plan for Use and Dissemination is presented in a separate confidential report as the deliverable of task 8.2.

The dissemination of results through spin-off companies, patents conferences, workshops and publications will attract new customers and target applications that cannot be addressed by current technologies and materials. The generation of valuable IP will be a key aspect in the long term and will generate licensing opportunities and spin-off potential. The final plan for exploitation and dissemination of knowledge from the DESYGN-IT project, based on the project outputs which have been reported at the final consortium meeting is presented in a separate report.

The major DESYGN-IT results with immediate commercial value that members of the consortium have reported are:

- 2 spin out companies
- 7 patents granted
- 11 patent applications
- Plans for more patents applications
- Commercial negotiations with a company, outside of the consortium, to implement the technology of the project in a new product.
- Talks with one of the world's largest polymers companies, to exploit the DESYGN-IT results in a project to study Polyolefin CNT composites.

The list of dissemination activities has been enhanced with the activities that took place in the final six months of the project and revised regarding the activities planned for the beyond the project life. A summary of the dissemination activities that the partners in the consortium have participated in during the lifetime of DESYGN-IT are:

- More than 50 Conferences reaching academic and industrial audiences of between 60 - 10000.
- 8 Workshops reaching academic and industrial audiences of between 15 - > 250.
- More than 15 Exhibitions and Trade shows aimed at Industry with attendances of between 300 and 55000.
- 7 Press Releases
- 2 Newsletters and flyers
- 1 Video Clip released to the general public
- 6 Websites, with links to more than 50 websites hosting papers from the DESYGN-IT project
- Participating in 25 National and EU Collaborative Projects
- Members of 10 Policy and Standards group
- Funded the studies of 18 PhDs, 2 MSc, 5 Trainees and 4 Engineers

Website & Logo:

The project public website can be accessed through
http://www.tcd.ie/Physics/DESYGNIT/index.php

The area of the website accessible to the public outlines the project objectives and the consortium members. The website will be developed further to include all publishable results of the project, links to the sites of similar framework projects and a counter to monitor the level of interest in the site. Work has been done to have links to the DESYGN IT on other related websites and to date more than fifty websites link to the DESYGN IT website.

The logo, for the DESYGN project, has been developed for some time now; see above. This appears on all the DESYGN IT publishable material. It has been used on the following media: reports, slides, website, brochures and posters.

The templates, available on the Cordis website, for gathering information on the dissemination activities for FP^ projects were used throughout the project. The information provided by all the partners of the DESYGN IT consortium has been collated and presented here as:

1. **Targeted Events (Ongoing)**
2. **Collaborations**
3. **Knowledge & Skill Generation with EU Research institutes and SMEs**
4. **Publications**
   - **Published Papers**
   - **Publications – In preparation:**
   - **Invited Talks and Presentations**
   - **Posters**

Targeted Events (Ongoing)

Related Meetings, Conferences and Workshops attended/to be attended by DESYGN IT partners.

Month	Partner	Event	Type of Audience
Year		**2004**	
Media Activity			
Oct	MSU	Daily press. Sundsvalls tidning 2004-10-19 ”Nanoteknologi ger ingenjörer	General public
Year		**2005**	
Conference			
	MSU	Gothenburg, Sweden	Research
Jan	IJS	The 1st International Conference on Nanomaterials, Taipei, Taiwan	Research
Feb	IJS, TCD, MO6	NanoTech insight : [the International Conference on Nanotechnology: Science and Applications], Luxor	Research
Mar	IJS,MO6	XIXth International Winterschool Euroconference on Electronic Properties of Novel Materials, Kirchberg/Tirol, Austria.	Research
Apr	UU	Opto-Ireland, Royal Dublin Society, Ireland.	Academic/Industry
	TCD	World Nano-Economic Congress (WNEC), Dublin, Ireland.	Industry
May	MSU	Nordic Microscopy Society Meting, SCANDEM, Göteborg, Sweden	Academic/Industry
	TCD	European Materials Research Society Spring Meeting STRASBOURG France	Industry
	UU	8th International Conference on Applications of Diamond and Related Materials/ 1st Nanocarbon Joint Conference, Argonne National Laboratory, Chicago, USA.	Industry
Jun	MO6	IX Conference and Exhibition of the European Ceramic Society, Portorož, Slovenia	Academic/Industry
	MSU, UCC	NT’05: 6th International Conference on the Science and Application of Nanotubes, Göteborg University, Sweden.	Academic/Industry
	QUB	Sixth International Conference on the Science and Application of Nanotubes Gothenburg, Sweden	Industry
	UU	Proceedings of SPIE Volume: 5824 Opto-Ireland June: Nanotechnology and Nanophotonics	Industry
	QUB , UCAM-DENG	6th International Conference on the Science and Applications of Nanotubes, Göteborg, Sweden	Research

Month	Partner	Event	Type of Audience
Jul	UCAM	International Conference on Materials for advanced Technologies, ICMAT Singapore	Academic/Industry
	IJS	[International conference on] Quantum Transport in Synthetic Metals & Quantum Functional Semiconductors, Bologna, Italy	Research
Aug	UCAM-DENG	16th International Symposium on Plasma Chemistry (ISPC), Toronto, Canada.	Academic/Industry
Sep	MSU	IASEM, Cuba	Academic/Industry
	UCAM	21st International Conference on Amorphous and Nanocrystalline Semiconductors (ICANS), Lisbon, Portugal. Talk: Carbon Nanotubes for Electronic Transport applications.	Academic/Industry
Oct	IJS, TCD	4th Symposium of science and technology of nanomaterials in Slovenia	Research
Nov	QM	Young Physicists' Conference, Trinity College Dublin. Poster Presentation	Academic/Industry
	MSU	Materials Research Society (MRS), Boston, USA. Academic	Industry
Exhibition			
	FhG	NanoSolutions	Industry
	FhG	MOTEK	Industry
Trade Show			
Nov	FhG	Nanosolution (NanoRoadMap Conference for European Industry), Köln, Germany	Academic/Industry
Workshop			
May	MSU	Nordic Microscopy Society Meting, SCANDEM, Göteborg, Sweden	Academic/Industry
Sep	MO6	1st workshop of the INTERREG IIIA SLO-ITA project: Advanced methods for novel materials. Trieste, Italy.	Academic/Industry
Year		**2006**	
Conference			
	MSU	16th International microscopy congress, Sapporo, Japan	Research
	MSU	Istanbul, Turkey	Research
Jan	UCAM-DENG	NanoSingapore 2006: IEEE Conference on Emerging Technologies – Nanoelectronics, Singapore. Poster: Rapid thermal chemical vapour deposition of single-wall carbon	Academic/Industry
	FhG	Actuator	Industry
	UCAM-DENG	NanoSingapore 2006: IEEE Conference on Emerging Technologies - Nanoelectronics News Singapore,	Research
Mar	NTERA	Society for Information Display (SID) Mid-	Academic/Industry

Month	Partner	Event	Type of Audience
		European Chapter, Eindhoven, Netherlands.	
	UL	2nd Latvian conference "Functional materials and nanotechnologies", Riga, Latvia.	Industry
	IJS	XXth International Winterschool Euroconference on Electronic Properties of Novel Material, Kirchberg, Tirol, Austria s	Research
Apr	NTERA	Printed Electronics Europe 2006 (an IDTechEx event), Cambridge, UK.	Academic/Industry
May	FhG	European Materials Research Society (EMRS), Nice, France. Working title: "Simulation of CNT-Actuation	Industry
	UCC, TCD	European Materials Research Society (E-MRS) Meeting, , Nice, France	Research
	TCD	Nanoparticles for European Industry: Manufacture, Scale-up, Stabilization, Characterization and Toxicology, The Olympia Conference Centre	Research/Industry
	TCD, QUB	2006 NSTI Nanotechnology Conference and Trade Show - Nanotech 2006 9th annual NSTI Nanotech 2006, May 7-11, Hynes Convention Center, Boston Massachusetts	Research/Industry
Jun	UCAM-DENG	3rd IUPAC-sponsored International Symposium on Macro- and Supramolecular Architectures and Materials(MAM) , Tokyo (Invited Talk)	Research/Industry
Jul	MSU, QUB, UU	International Conference on Nanoscience and Technology (ICN+T), Basel, Switzerland	Industry
	QUB	14th International Conference on Composites/Nano Engineering (ICCE), Boulder Colorado USA	Industry
	ALL	International Conference on Synthetic Metals (ICSM), Trinity College Dublin	Research and Industry
Aug	FhG	The International Society for Optical Engineering (SPIE), San Diego, California	Academic/Industry
	UL, NUIC, IJS, QM	International Conference on Nanoscience and Technology, Basel, Switzerland	Public/Academic
	QUB , UCAM-DENG	ICNT06, incorporating STM06 – International Conf. on Scanning Tunnelling Microscopy and Applications	Research
	UL	International Conference on Nanoscience and Technology, Basel, Switzerland	Research and Industry
Sep	FhG	10th International Conference on Plasma Surface Engineering (PSE), Garmisch-Partenkirchen, Germany.	Academic/Industry
	QUB	Materials Research Society (MRS), San Francisco, USA.	Industry
Nov	QUB	American Chemical Society Meeting & Exposition	Industry

Month	Partner	Event	Type of Audience
		(ACS), San Francisco, USA.	
Event			
May	NUIC	The E-MRS 2007 Spring Meeting was held in Nice, France	Research/Industry
Exhibition			
	FhG	MOTEK	Industry
	FhG	NanoEurope	Research/Industry
	FhG	Actuator	Research/Industry
	FhG	NanoSolutions	Industry
Oct	MSU	Nanotech forum, Stockholm, Sweden	Industry
	TG	Glasstec	Industry
Media Activity			
	FhG	Video Clip	General public
	FhG	Fraunhofer Magazine	General public
Mar	TCD	Magazine Article Title Nanotechnology : Industry-scale Nanotube Production Technology Ireland, Issue 1, Vol 37, March/April 2006,	General public
Oct	UL	Press release - 3 October	General public
Nov	UL	Press release - 29 November	General public
Seminar			
	TG	Annual Toughglass Technical Seminar.	Academic/Industry
Sep	TG	Safety Glazing, UK	Industry
Trade Show			
Feb	FhG	5th International Workshop on Biomedical Applications of Nanotechnology (NanoMed), Berlin, Germany.	Academic/Industry
	FhG	International Nanotechnology Exhibition and Conference (Nanotech), Tokyo, Japan.	Academic/Industry
May	NTERA	Adria, Germany	Industry
Jun	NTERA	Society for Information Display (SID) International Symposium, San Francisco, USA.	Academic/Industry
Workshop			
Jan	TCD	ICON: International Council on Nanotechnology: European Workshop on International Collaboration on Nanotechnology Environmental Health & Safety	General public
Feb	TCD	Hosted 3-day “Carbon Nanotube Workshop” for Intel Ireland Ltd	
Jul	TG	Toughglass Workshop, Dublin	Academic/Industry
	ALL	1st DESYGN IT nanotube workshop (ICSM), Trinity College Dublin	Research and Industry
Oct	QM	Quantum Physics of Nanostructures, Stratford-Upon-Avon	Research

Month	Partner	Event	Type of Audience
	UL, NUIC	The 5-th ESF-Nanotribology Workshop, Antalya, Turkey	Research
Oct	TCD, UU	US-Ireland R&D Partnership Nanotechnology Workshop Ramada Hotel, Belfast, NI. The US, Ireland and Northern Ireland have come together for a unique initiative to increase the level of collaborative R&D amongst researchers and industry across the three jurisdictions that will generate innovations to the marketplace and lead to improvements in healthcare, disease prevention and other technologies	Research/Industry
Oct	UU	Nanoscience Ireland event, Ramada Hotel, Belfast.	Scientific funding agencies
Other Activities			
Sep	UL	Popularization activity “Scientific Night”	General public
Year		**2007**	
Conference			
	FhG	SPIE	Research
Jan	TCD, UU	Advanced Nanomaterials IIT Bombay, India	Research and Industry
Feb	UCAM-DENG	Fall MRS, Warsaw	Research/Industry
Mar	UU	IOP conference: Nanoscale Physics and Technology-the interface with medical and biological Science, , University of Southampton, UK	Research
Apr	ST&D	ENGINEERS IRELAND ANNUAL CONFERENCE 2007	Industry
	UL, NUIC	International Baltic Sea Region Conference „Functional materials and nanotechnologies, Riga, Latvia	Research
	UCAM-DENG	Italian Vacuum Society meeting, Florence (Invited Talk)	Research/Industry
	UL	International Baltic Sea Region conference "Functional materials and nanotechnologies", Riga, Latvia	
May	QUB	Polymer Processing Society, 23rd Annual Meeting, Salvador, Brazil	Research
Jun	QUB , UCAM-DENG	Surface Plasmon Photonics 3, Dijon, France	Research
Jul	UU	International Conference on Materials for Advanced Technologies (ICMAT 2007), Singapore	Research and Industry
	MSU, UL,	International Conference on Nanoscience and	

Month	Partner	Event	Type of Audience
	NUIC	Technology (ICN+T 2007), Stockholm, Sweden	
	UL, NUIC	International Conference on NanoScience and Technology, Stockholm, Sweden,	Research and Industry
Aug	UCAM-DENG	SMN, China (Invited Talk)	
Sep	QM	Trends in Nanotechnology, San Sebastian, Spain	Research
	TCD	Conference on Laser Ablation (COLA), Tenerife, Spain	Research
	UL, NUIC	European Congress on Advanced Materials and Processes, Nűrnberg, Germany	Research and Industry
Oct	IJS	SLONANO 2007, Ljubljana, Slovenia	
Nov	UL	4th International conference on nanotechnologies NANOVED, Bratislava, Slovakia.	
Dec	TCD	3rd International Conference on Nanomaterials and Nanomanufacturing, CRANN, Trinity College, Dublin	Research
Event			
Jan	TCD	FP7 – NMP Launch, Dublin. Ireland	Industry and Research
	TCD	FP7 Brokerage events in Ireland and Austria.	Industry and Research
Feb	UCAM-DENG	TMS, ORLANDO, FLORIDA	Research/Industry
Jun	TCD	E-MRS 2007 Spring Meeting , Strasbourg, France	Research and Industry
Jul	TCD	ERA Green Paper Consultation	Research
Sep	TCD, NUIC, UL	European Congress and Exhibition on Advanced Materials and Processes, Euromat 2007, Nürnberg, Germany	
Exhibition			
	FhG	Hannover Messe Internationala	Industry
	FhG	Kirchentag	General Public
	FhG	MiNat	Industry
	FhG	Farbe	Industry
	FhG	NanoEurope	Research/Industry
	FhG	NanoSolutions	Industry
Media Activity			
Mar	MSU	Daily press, Sundsvalls tidning 2007-03-16, “Studenter ser atomer	General public
Apr	MSU	Daily press, Sundsvalls tidning 2007-04-26, “Ide-sprutor vinner pris	General public
Nov	TCD	Joint Press release with AzZojono Journal of Nanotechnology Online publicising DESYGN-IT Special Edition - has led to more than 50 website	General public

Month	Partner	Event	Type of Audience
		appearances of DESYGN IT	
Workshop			
Nov	All	2nd DESYGN IT nanotube workshop : The Octagon, Queen Mary, University of London	Research and Industry
Trade show			
Nov	TG	Glass Processing and Technologies, Birmingham, UK. - Samples to be demonstrated.	Academic/Industry
Feb	NTERA	Flexidis Workshop, UK	Industry
May	UL, NUIC	6th ESF Nanotribology Workshop, Santa Margherita di Pula, Italy	
Jul	UL	4th International Workshop on Nanosciences and Nanotechnologies NN07, Thessaloniki, Greece	
Other Activities			
Feb	UL	Presentation at Intel seminar in Ireland	Industry
Aug	NTERA	Business development discussions with manufacturing partner in US	Industry
Nov	NTERA	Business development discussions with manufacturing partner in UK	Industry
Dec	NTERA	Business discussions with manufacturing partner in Switzerland	Industry
Year		**2008**	
Conference			
Jan	ST&D	2nd International Meeting on Developments in Materials, Processes and Applications of Nanotechnology, Cambridge 2007	Research/Industry
Mar	QM	International Winterschool on Electronic Properties of Novel Materials, Kirchberg, Austria	Research
Jun	FhG	ACTUATOR International Conference and Exhibition on New Actuators and Drive Systems	Research/Industry
Media Activity			
Jan	TCD	Newsletter - Intertechpira - Nanomaterial news vol 3 Iss 20	General public
Other Activities			
	MSU	Website www.miun.se/personal/hakan.olin , In-situ TEM probing movies at http://www.tfm.miun.se/~maghum/Desygn-IT.htm	General public
	TCD	Produced flyer for distribution by partners.	General public
	TCD	DESYGN-IT website	General public
	TG	Ongoing - Possibility of integration in non-scientific reviews in glass reference magazines.	Academic/Industry

Collaborations

Collaboration with EU projects / Memberships / Affiliations / involvement with industry or scientific organizations by DESYGN IT partners.

Collaboration		Contact		
Name	**Nature**	**Name**	**Point**	**Country**
NANOTEMP	TMR Network	M. Green	Oxford	UK
EREMON	Marie-Curie	D. Mihailovic	Ljubljana	Slovenia
CARB-ON-CHIP	Research	Jenny Patterson	Intel	IRE
NANOFIRE	Scientific exchange	Ton Peijs	QMC	Italy
Plasmo-Nano Devices, EC Network of Excellence, FP6-2002-IST-1-507879	Raman spectroscopy using nanowire substrates	L. Engand R. Pollard A. Dereux (co-ordin'r)	L. Engand R. Pollard A. Dereux	DE UK FR
PC/ABS CNT Composites	Exchange of PhD student for 2 months to exploit initial results from WP5 in DESYGN-IT with another polymer type	Professor Michele Modesti	University of Padua	Italy
Rheology of Polymer CNT Composites	Measurements to determine the rheological percolation of polymer CNT composites	Dr Petra Potschke	Leibniz Institute for Polymer Research	Germany
Polyolefin CNT Composites	Discussion group on application of WP5 results to Basell resins	Piet Roose	Basell	Belgium
SEBS CNT Composites	Preparation of SEBS CNT Composites	Professor Peter Halley	University of Queensland	Australia
Fraunhofer Verbund Nanotechnologie	Research	Dr. K. H. Haas	Munich	Germany
NANOMED	Development and Demonstration of a Carbon Nanotube Actuator For Use in Medical Technology	Ray Hodgkinson	Sevenoaks	UK / EC / EU
CarNak	Fraunhofer internal research project	Dieter Sporn	Munich	Germany
CANDICE	EU	Pribat, Didier	+33-1-69333685	France
CANAPE	EU	Robertson, John	+44-12-23332689	UK
NANORAC	EU		rtd-nanotech@cec.eu.int	

Collaboration		Contact		
Name	**Nature**	**Name**	**Point**	**Country**
Nanotechnology for the forestry industry	University – Industry Mid Sweden, Obducat AB (nanotech company) & Permascand (forest industry). Funding KK-foundation and Swedish Research Council University	H. Olin	MSU	Sweden
Printed RFID Sensor Solutions Funding Vinnova	Mid Sweden Univ, KTH, and VTT Finland + 10 companies	H-E. Nilsson, H. Olin	MSU	Sweden
MTKD-CT-2004-014484. NANOCHROMICS - Development of Advanced Electronic Paper-like Display Technologies.	Marie Curie Transfer of Knowledge. TOK – Dev	Sarah Little	NTERA	Ireland
MTKD-CT-2006-042763. NANOMATRIX - Innovation of Novel High Resolution Electronics for Reflective Electrochromic Display	Marie Curie Transfer of Knowledge.	Sarah Little	NTERA	Ireland
EU 7th Framework NMP Program Committee	Committee member	D. Erts	UL	Latvia
COST	Domain: Materials, Physical and Nanosciences	D. Erts	UL	Latvia
FP6-2004-TI-4-033205 IPMMAN	Improvement of Industrial Production Integrating Macro-, Micro- and Nanotechnologies	A. Almansa D. Erts	Profactor UL	Austria Germany Griece Italy Isarael Latvia Spain Portugal Hungary Romania Russia UK
EU COST project P13 (MOLSIMU):	Forging the Missing Link: from Molecular Simulations to Nanoscale Experiments	P. Nielab (D. Erts)	Univ. Konstanz (UL)	DE AT, BE, DK, EE, FI, FR, HU, IL,

Collaboration		Contact		
Name	**Nature**	**Name**	**Point**	**Country**
				IT, LV, NL, PT, RO, ES, SE, UK
Modern functional materials for micro-electronics, nanoe-lectronics, biomedicine and constructive composites	Latvia national program in material sciences: participation in 2	D. Erts	UL	Latvia
Chierarchial nano architectures and nanodevices”	ERAF projects	D. Erts	UL	Latvia
Nanomaterials and nanotechnologies	Latvia Council of Science cooperation project	A. Sternbergs D. Erts	UL	Latvia
Development of Technologies for Production of Nano porous materials	Latvia Council of Science project	D. Erts	UL	Latvia
Properties of individual nanoelements	Latvia Council of Science project	D. Erts	UL	Latvia
Compatible inorganic & molecular nanocomponents for bio and nanotechnologies	Project of University of Latvia	D. Erts	UL	Latvia
Glazing Executive	Chairman	John Agnew	Glass and Glazing Federation	UK
ISO Committee	Standards for Curved Glass	Steve Rice	Glass and Glazing Federation	UK
Experts" producing the vocabulary for a "Publicly Available Specification" on carbon nanostructures	British Standards Institute	W. Milne	UCAM-DENG	UK
NanoICT	CA to reinforce and support the whole European Research Community in “ICT nanoscaledevices	Dr. Antonio Correia	PHANTOMS Foundation	Spain
Nanotechnology Taskforce	Task Force to encourage debate about the use and the potential of nano technology in the UK	Nick Bishop	nbishop@mantra-pr.com	UK

Knowledge & Skill Generation with EU Research institutes and SMEs

Student	Degree or award	Area of knowledge
Björn Högberg	PhD (2007)	Programmed self-assembly
Caroline McClory	PhD (2007)	Melt Processed Polymer Carbon Nanotube Composites
Christine Malmgren	Licentiate planned Dec 2008	TEM, nanowires
Daire Cott	PhD	Chemistry
Daniel Selig	Trainee (2005/2006)	Performance of Bucky Paper measurements.
David Faller	Dipl.-Ing (2006)	Comparison of the results and continuation of the research about the actuation of Bucky Paper and CNT Composites. (In German)
Duong Thi-Thu-Thao	Laboratory skills (2005-2007)	Production of bucky paper
Enrique Sterling	PhD Planned (2008)	Laser deposition of thin films
Eric Stephane Mepfue	Trainee (2004/2005)	Actuation and resistance measurements of carbon nanotube sheets (bucky paper).
Fiona Blighe	PhD(2008)	Carbon Nanotube polymer composites
H. Murphy	PhD (December 2006)	Bioelectronic detection employing carbon nanotubes
Henning Riedel	Dipl.-Ing. (2006)	Analysis and optimization of carbon nanotubes for their employment in actuating systems. (In German)
Jaideep Kulkarni	PhD	Chemistry
Jose Duenas	PhD (2006) Thesis embargoed until 2009 to protect results.	Surface enhanced Raman scattering using optical antennae based on substrates with vertically aligned multi-walled carbon nanotubes.
Ju Xu	PhD	Chemistry
Jure Strle	PhD (….)	Measurements and manipulation of MoSIx nanowires under AFM and c-AFM
Kristine Bedner	Dipl.-Ing. (2005)	Analysis and optimization of carbon nanotubes for their employment in actuating systems. (In German)
Lina Rustam	Trainee (2005/2006)	Preparation of Bucky Papers.
M. McMullan	PhD (to submit in Sept 2008)	Bioelectronic detection employing carbon nanotubes and MoSi nanowires

Magnus Hummelgård	PhD planned dec 2008	In-situ TEM probing, carbon nanotubes, nanowires
Maria Ljusanin	Dipl.-Ing. (2007)	Investigations on the reproducibility of potential and charge-controlled movement behaviour of carbon nanotube actuators. (In German)
Mark Mann	PhD planned 2008	Production of arrays of nanotubes for field emission
Marko Uplaznik	PhD (2008)	MoSIx nanowire circuits
Markus Hoffman	Trainee (2007)	Performance of Bucky Paper measurements.
Markus Schäfer	Trainee (2005)	production of bucky paper
Mihaela Ploscaru	PhD (2008)	Fictionalization of MoSIx nanowires
Primoz Kusar	PhD (2007)	Time-resolved ultra-fast measurements of MoSIx nanowires
Sharvari.Dalal	PhD 2008	Production of CNTS for SERS measurements
Simone Hettler	Trainee (2005)	production of CNT dispersions
Stephen Hudziak	PhD	Nanomaterials synthesis and characterisation
Tim Butler	PhD submitted 2008	Nanolithography
Tony Donnelly	PhD planned (2008)	Laser ablation
Trevor Woods	MSc planned2009c	CNT polymer composites
Urszula Kosidlo	MSc (2007)	Optimization of CNT actuators
Vinh Huynh	Trainee (2004/2005)	Carbon Nanotubes and their applications. Development of new test set-up.
Yvonne Köhne	Laboratory skills (2004-2006)	Production of bucky paper and characterisation

Publications

Published Papers

Rory W. Leahy, Emer Lahiff, Andrew I. Minett, Werner J. Blau. 'Chemical Vapour Deposition Grown Carbon Nanotubes for Interconnect Technology'. *AZojono Journal of Nanotechnology Online, DESYGN-IT Special Edition, November 2007*

Emer Lahiff, Kentaro Nakajima, A.I. Minett, W. J. Blau. 'Producing controlled grid patterns of nanotube arrays for strengthening polymer composites' *AZojono Journal of Nanotechnology Online, DESYGN-IT Special Edition, November 2007*

Cott, D. J.; Petkov, N.; Morris, M. A.; Platschek, B.; Bein, T.; Holmes, J. D. 'Preparation of oriented mesoporous carbon nano-filaments within the pores of anodic alumina membranes' *J. Am. Chem. Soc., 128, 3920-3921.*

Žumer, Marko, Nemanič, Vincenc, Zajec, Bojan, Remškar, Maja, Ploscaru, Mihaela, Vengust, Damjan, Mrzel, Aleš, Mihailović, Dragan. 'Field emission of point-electron source Mo6S3I6 nanowires'. *Nanotechnology (Bristol), vol. 16, p. 1619-1622 (2005)*

Joly-Pottuz, L., Dassenoy, F., Martin, J. M., Vrbanić, Daniel, Mrzel, Aleš, Mihailović, Dragan, Vogel, W., Montagnac, G. 'Tribological properties of Mo-S-I nanowires as additive in oil' *Tribol. lett., vol. 18, no. 3, pr. 385-393 (2005).*

Paglia, Gianluca, Božin, Emil S., Vengust, Damjan, Mihailović, Dragan, Billinger, Richard. 'Accurate structure determination of Mo6SyIz nanowires from atomic pair distribution function (PDF) analysis' *Chem. mater. [Print ed.], vol. 18, pr. 100-106. ().*

Vengust D., Pfuner F., Degiorgil., Vilfan I., Nicolosi V., Coleman J.N., Mihailović D., 'Optical properties of $Mo_6S_3I_6$ nanowires' *Phys. Rev. B* **76** (7) art. no. 075106, (2007)

Berčič Boštjan, Pirnat Urša, Kuša Primož, Dvoršek Damjan, Vengust Damjan, Mihailović Dragan 'Resistivity measurements of Mo6S3I6 nanowires networks' *Phys. status solidi, b Basic res. , vol. 243, no. 13, p. 3306-3310. ().*

Ploscaru, Mihaela, Jenko, Saša, Uplaznik, Marko, Vengust, Damjan, Turk, Dušan, Mihailović, Dragan. 'Force spectroscopy measurements of MoSIx nanowires with functionalized molecules'. *Phys. status solidi, b Basic res., vol. 243, no. 13, p. 3325-3328 ().*

Bercic B., Pirnat U., Kusar P., Dvorsek D., Mihailovic D., Vengust D., Podobnik B., 'Transport properties of Mo6S3I6 nanowire networks', *Appl. Phys. Lett. 88, p. 173103-1-3, ().*

Uplaznik M., Bercic B., Strle J., Ploscaru M., Dvorsek D., Kusar P., Devetak M., Vengust D., Podobnik B., Mihailovic D., 'Conductivity of single $Mo_6S_{9-x}I_x$ molecular nanowire bundles', *Nanotechnology 17, 5142-5146, ().*

Vilfan, Igor, Mihailović, Dragan. 'Nonlinear elastic and electronic properties of Mo6S3I6 nanowires'. *Phys. rev., B, Condens. matter mater. phys., vol. 74, p. 235411-1-235411-7 ().*

Kušar, Primož, Mihailović, Dragan. 'Sound propagation in a highly damped Mo6S3I6 nanowire network measured by femtosecond pump-probe spectroscopy'. *J. appl. physi., vol. 102, no. 1, p. 013510-1-013510-3 (2007).*

Dvoršek, Damjan, Vengust, Damjan, Nicolosi, Valeria, Blau, Werner J., Coleman, J. C., Mihailović, Dragan. 'Structural and physical properties of Mo6SxI(9-x) (4.5<x<6) molecular.' *J. nanosci. nanotechnol. 2007, (published* http://dx.doi.org/10.2240/azojono0124)

Vengust, Damjan, Pfuner, F., Degiorgi, L., Vilfan, Igor, Nicolosi, Valeria, Coleman, Jonathan N., Mihailović, Dragan. 'Optical properties of Mo6S3I6'. *Phys. rev., B, Condens. matter mater. phys., no. 7, p. 075106-1-075106-7 (2007).*

Lasjaunias, J. C., Sulpice, A., Biljaković, K., Vengust, Damjan, Mihailović, Dragan. 'Low-energy vibrational excitatins of Mo6S3I6 nanowires revealed by low-temperature specific heat'. *Nanotechnology (Bristol) , vol. 18, p. 355704-1-355704-7 (2007).*

Kis, András, Csanyi, G., Vrbanić, Daniel, Mrzel, Aleš, Mihailović, Dragan, Kulik, A. J., Forró, László. 'Nanomechanical investigation of Mo6S(9-x)Ix nanowire bundles'. *Small (Weinh., Print), , vol. 3, no. 9, p. 1544-1548 (2007).*

Dvoršek Damjan, Žumer Marko, Nemanič Vincenc, Mihailović Dragan, Vengust Damjan. 'Growth and field emission properties of vertically aligned molybdenum-sulphur-iodine nanowires on molybdenum and quartz substrates.' *J. appl. physi. , vol. 102, no. 11, p. 114308-1-114308-5., (2007).*

Ploscaru Mihaela, Jenko Saša, Uplaznik Marko, Vengust Damjan, Turk Dušan, Mrzel Aleš, Mihailović Dragan, 'Mo6S(9-x)Ix nanowire recognitive molecular-scale connectivity'. *Nano lett. vol. 7, no. 6, p. 1445-1448, (2007).*

Gamal Abbas, Pagona Papakonstantinou*, Ganjigunte R.S Iyer, Ian W. Kirkman, Li C. Chen, 'Substitutional Nitrogen Incorporation through RF Glow Discharge Treatment and Subsequent Oxygen Uptake on Vertically Aligned Carbon Nanotubes', *Physical Review B 75 (2007) 195429.*

U. Vohrer, J. Holmes, Z. Li, A. The, P. Papakonstantinou, M. Ruether, W. Blau, 'Tailoring the wettability of carbon nanotube powders, bucky papers and vertically aligned nanofibers by plasma assisted functionalization' , *Azojono, Journal of Nanotechnology online,* http://www.azonano.com/oars.asp

Z. Li, P. Papakonstantinou, J. M. Tobin, K. Wang, U. Vohrer, M.A. Morris, S. Kumar, G. Attard, J.D. Holmes*, 'Supercritical fluid growth of porous carbon nanocages', *Chemistry of Materials, 19 (2007) 3349.*

A. Erdem, P. Papakonstantinou*, H. Murphy, 'Direct DNA hybridization at disposable graphite electrodes modified with carbon nanotubes', *Analytical Chemistry, 78 () 6656.*

H. Murphy, P. Papakonstantinou*, T.I.T. Okpalugo, 'Raman study of multiwalled carbon nanotubes functionalized with oxygen groups', *Journal of Vacuum Science and Technology B 24 () 715.*

U. Vohrer, N. P. Zschoerper, Y. Koehne, S. Langowski and C. Oehr, P*lasma Processes and Polymers 4 (2007) S871.*

U. Kosidlo, D-G. Weis, K. Hying, M.H. Haque, I. Kolaric *'Development of Measurement Set-up for Electromechanical Analysis of Bucky Paper Actuators' AZojono Journal of Nanotechnology Online, DESYGN-IT Special Edition, November 2007* http://www.azonano.com/Details.asp?ArticleID=2043

M. Baxendale, M. Melli, Z. Alemipour, I. Pollini, T.J.S. Dennis, 'Quantum Conductance in Single- and Double-Wall Carbon Nanotube Networks' *J. Appl. Phys. 102, 103721, 2007*

R. Zhang, M. Baxendale, T. Peijs, 'Universal Resistivity-Strain Dependence of Carbon Nanotube/Polymer Composites' *Phys. Rev. B 76, 195433, 2007*

K. Svensson, H. Olin, E. Olsson, 'Nanopipettes for metal transport', *Physical Review Letters, 93 (2004) 145901*

A. Nafari, P. Enoksson, H. Olin, A. Danilov, and H. Rodjegard, 'A micromachined nanoindentation force sensor', *Sensors and Actuators A 123 (2005) 44-49*

B. Högberg, J. Helmersson, S. Holm, and H. Olin 'Study of DNA coated nanoparticles as possible programmable self-assembly building blocks' *Applied Surface Science 252 () 5538-5541*

B. Högberg and H. Olin, 'Programmable self-assembly – Unique structures and bond uniqueness', *J. Comput. Theor. Nanoscience 3 () 391-397*

B. Högberg and H. Olin, 'Anisotropically DNA-functionalized nanoparticle dimmers', *Eur. Phys. J. D 43 (2007) 299-302*

Ph.D. Thesis, Bjorn Hogberg, 'DNA-mediated self-assembly of nanostructures', *Mid Sweden University (2007)*

D. Erts, A. Lohmus, J. D. Holmes, H. Olin. 'Probing of nanocontacts inside a transmission electron microscope'. *Chapter in book "Fundamentals of Friction and Wear on the Nanoscale", Springer (2007)*

Z.. Li, J. Andzane, D. Erts, J. Tobin, K. Wang, M.A. Morris, G. Attard, J.D. Holmes, 'A New Supercritical Fluid Method for Growing Carbon Nanotubes', *Advanced Materials, 19, 3043–3046 (2007).*

J. Andzane, J. M. Tobin, Z. Li, J. Prikulis, M. Baxendale, H. Olin, J. D. Holmes, D. Erts. 'Selection of Application Specific Single and Multi-walled Carbon Nanotubes by in Situ Characterization of Conductive and Field Emission Properties'. *AZojono: Journal of Nanotechnology Online, (2007) DOI 10.2240/azojono0123*

Publications – In preparation:

Fiona M Blighe, Yenny R Hernandez, Werner J Blau and Jonathan N Coleman 'Observation of percolation like scaling far from the percolation threshold in high volume fraction polymer-nanotube composite films'

Li, Z.; Zhang, H.; Tobin, J. M.; Qiu, J.; Attard, G.; Holmes, J. D. 'Synthesis of bamboo-structured carbon nanotubes on MgO supported Mo/Cu catalysts' *Diamond and Related Materials* , submitted.

Li, Z.; Andzane, J.; Erts, D.; Tobin, J. M. Wang, K.; Attard, G. Holmes, J. D. 'Supercritical fluid growth of high quality carbon nanotubes'

Li, Z.; Papakonstantinou, P.; Tobin, J. T.; Wang, K.; Vohrer, U.; Morris, M. A.; Attard, G.; Shailesh Kumar, S.; Holmes, J. D. 'Supercritical Fluid Growth of Porous Carbon Nanocages'.

N. Sun, M. McMullan, P. Papakonstantinou*, D. Mihailovic, M. Li, Amplified electrical and optical detection of proteins derived from Mo6SxI9-x nanowires' submitted

N. Sang*, P. Papakonstantinou, J. McLaughlin, W. C. Chen and L. C. Chen, 'Growth of tabular graphite cones on si substrate and field emission properties', submitted

M. Baxendale, S. Hudziak, A. Darfeuille, 'Magnetoconductive carbon nanotube/polymer composite'

M. Baxendale, H. Olin, M. Hummelgard, 'Quantum conductance of carbon nanotube systems: direct imaging'

M. Baxendale, A. McNally, 'Quantum conductance of functionalised carbon nanotube systems'

C. McClory1, T. McNally, M. Baxendale, P. Potschke, W. Blau, M. Reuther, 'Electrical and Rheological Percolation of PMMA MWCNT Composites'. *Submission to Macromolecules*

C. McClory, T. McNally, P. Potschke, 'Polystyrene Multiwalled Carbon Nanotube Composites', *submission to Polymer*

C. McClory, T. McNally, M. Billham, P. Hornsby, 'Melt Processing Behaviour of Polyethylene MWCNT Composites' *submission to European Polymer Journal*

C. McClory, T. McNally, Peter Halley, Darren Martin, Michael Murphy, 'Styrene-ethylene/butylene-styrene block copolymer MWCNT Composites' *submission to Journal of Applied Polymer Science*

JA Duenas, MG Boyle, SEJ Bell, P Dawson, A-S Teh, KBK Teo, WI Milne, 'Optical antenna amplification of Raman signal from vertical, multi-walled carbon nanotubes',: *NanoLett or Appl. Phys. Lett.Submission imminent (Jan/Feb 08)*

JA Duenas, MG Boyle, SEJ Bell, P Dawson, A-S Teh, KBK Teo, WI Milne, 'Surface enhanced Raman scattering from vertically-aligned, silver-dressed multi-walled carbon nanotubes acting as optical antenna structures', *Chem. Phys. Lett. or possibly Nature Materials Submission Feb/Mar 08*

'Use of carbon nanotube tip as optical antenna in light emission from scanning tunnelling microscope' *NanoLett or Appl. Phys. Lett. Submission May/Jun 08 pending acquisition of further results*

P. Kumari, S. S. Roy and J. A. McLaughlin, 'Growth and characterization of zinc oxide nanoneedles': *(Submitted to Journal of Nanoscience and Nanotechnology).*

A. Mathur, M. Tweedie, S. S. Roy, P. D. Maguire and J. A. McLaughlin, 'Electrical and Raman spectroscopic studies of vertically aligned multi-walled carbon nanotubes': *(Submitted to Journal of Nanoscience and Nanotechnology).*

N. Soin, S. S. Roy, P. D. Maguire and J. A. McLaughlin, 'Effect of catalyst thickness and excitation wavelength dependence Raman studies of aligned multi-walled carbon nanotubes': *(to be communicated to Journal of Raman Spectroscopy).*

P. Kumari, S. Kumar, A George, S. S. Roy and J. A. McLaughlin', Structural and field emission properties zinc oxide nanostructures': *(to be communicated to Journal of Applied Physics).*

A. Nafari, D. Karlen, C. Rusu, K. Svensson, H. Olin, P. Enoksson, 'MEMS sensor for in situ TEM atomic force microscopy', *J. Microelectromechanical Systems (2008) to appear*

B. Högberg, J. Boo, J. Liu-Helmersson, , L. Glans, and H. Olin, 'Programmable self-assembly: Theoretical aspects and DNA-linked nanoparticles', S*ystems Self-Assembly: Multidisciplinary Snapshots (2008) Elsevier, to appear*

'Nanorelay', *Planned for a scientific journal.*

'Electrical properties of Mo6 nanowires'. *Planned for a scientific journal.*

'In-situ probing histograms of carbon nanotubes'. *Planned for a scientific journal.*

'Enhancement of Raman modes of silver-capped and –coated vertically aligned carbon nanotubes', *intended for Chem. Phys. Lett.*

'Silver-dressed, vertically aligned carbon nanotubes as highly efficient substrate for surface enhanced Raman scattering', *intended for Nano Letters or Nature Nanotechnology*

Invited Talks and Presentations

Andžāne, J.; Prikulis, J.; Baxendale, M.; Holmes, J. D.; Erts, D. 'Conductivity, field emission and mechanical properties of carbon nanotubes' *2nd Latvian Conference on Nanomaterials and Nanotehnologies Riga, Latvia, March 27-28, 2006.*

J. Andzane, J. Prikulis, J. Tobin, Z. Li, J. D. Holmes, D. Erts. 'In situ investigation of Electrical Properties of Carbon Nanotubes Grown by Different Methods'. *International Baltic Sea Region Conference „Functional materials and nanotehnologies", p. 56, Riga, Latvia, 2 – 4 April 2007*

D. Erts, J. Andzane, J. D. Holmes. 'Nanoelectromechanical Devices Based on Nanowires and Nanotubes investigated by in Situ Techniques'. *6th ESF Nanotribology Workshop, p. 19, Santa Margherita di Pula, Italy, 13th – 16th May 2007*

J. Andzane, J. Prikulis, J. Tobin, Z. Li, J. Holmes, D. Erts. 'Structure dependent conductive and field emission properties of carbon nanotubes'. *International Conference on Nanoscience and Technology (ICN+T 2007), Stockholm, Sweden, 2-6 July 2007*

Andzane, J.; Tobin, J.; Li, Z.; Prikulis, J.; Holmes, J. D.; D. Erts, D. 'Conductive, field Emission and mechanical properties of carbon nanotubes grown by different methods'. *Euromat 2007, Nürnberg, Germany, 10-13 September 2007.*

Mihailović, Dragan, Mrzel, Aleš, Vrbanić, Daniel, Vengust, Damjan, Nicolosi, Valeria, Coleman, Jonathan N. 'MoSIx nanowires : a user-friendly new nano-materials'.

Mihailović, Dragan, Uplaznik, Marko, Ploscaru, Mihaela, Vengust, Damjan, Berčič, Boštjan. 'Functional properties of MoSIX nanowires'

Jenko, Saša, Ploscaru, Mihaela, Vengust, Damjan, Mrzel, Aleš, Gunčar, Gregor, Žerovnik, Eva, Brix, Klaudia, Mihailović, Dragan, Turk, Dušan. 'Immobilization of proteins onto MoSxIy nanowires'.

VRBANIĆ, DANIEL, PEJOVNIK, STANE, MIHAILOVIĆ, DRAGAN, KUTNJAK, Zdravko. 'Electrical conductivity of Mo6S3I6 and Mo6S(4.5)I(4.5)'.

Mihailović, Dragan. 'Functionality of MoSIx molecular nanowires: from magnetic molecular connectors to composites'

Dvoršek, Damjan, Berčič, Boštjan, Lasjaunias, J. C., Biljaković, K., Vengust, Damjan, Mihailović, Dragan. 'Thermodynamic and transport properties of Mo6S3I6 nanowire networks'.

Žumer, Marko, Nemanič, Vincenc, Zajec, Bojan, Remškar, Maja, Ploscaru, Mihaela, Vengust, Damjan, Mrzel, Aleš, Mihailović, Dragan. 'Field emission of point-electron source Mo6S3I6 nanowires'.

Ploscaru, Mihaela, Jenko, Saša, Uplaznik, Marko, Vengust, Damjan, Turk, Dušan, Mrzel, Aleš, Mihailović, Dragan. 'MoSIx nanowires functionalization for molecular-scale connectivity'.

Mihailović, Dragan. 'The holy grail in MoSI nanowires science and applications: electrical conductivity'.

'Bioelectronic Sensing – Interfacing Biological Molecules with Carbon Nanotubes for Sensing' *oral presentation in IOP conference: Nanoscale Physics and Technology-the interface with medical and biological Science, 26 - 27 March 2007, University of Southampton, UK*

G.Abbas, P.Papakonstantinou, S. Iyer, I. Kirkman, L.C. Chen, 'Substitutional Nitrogen Incorporation through RF Glow Discharge Treatment and Subsequent Oxygen uptake on vertically Aligned Carbon Nanotubes' *oral presentation at the International Conference on Materials for Advanced Technologies (ICMAT 2007), 1 - 6 July 2007, Singapore*

H. Murphy , P. Papakonstantinou , L.C. Chen, 'Sequence specific Label free DNA bioelectronic detection based on a semiconducting platform with vertically aligned carbon nanotubes', *oral presentation, at the International Conference on Materials for Advanced Technologies (ICMAT 2007), 1 - 6 July 2007, Singapore*.

'Direct Detection of Specific DNA binding using carbon nanotubes', *presented in Advanced Nano Materials 2007: An International Conference on Experimental Condensed Matter Physics, IIT Bombay, Jan 8-10 2007.*

'Carbon nanotubes: Growth, chemical and plasma Functionalization, spectroscopic verification and use in bioelectronic detection' *International conference of Micro and Nanotechnologies, ICMNT, 19-23 Nov, Tizi-Ouzou Algeria.*

'Direct DNA hybridisation at disposable graphite electrodes modified with carbon nanotubes', *International Conference of Science and Technology on Synthetic Metals, ICSM , 2-7 July , Dublin*

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