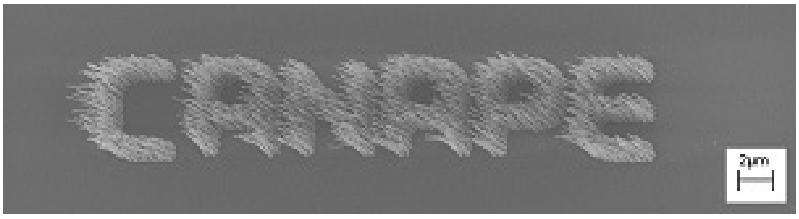

NMP4-CT-2004-500096

CANAPE

Carbon Nanotubes for Applications in Electronics, Catalysis, Composites and Nano-Biology

Integrated Project

Nanotechnologies, Materials, New Processes

12 Month Periodic Technical Report:

Publishable Summary

Period covered: 1 June 2006 to 31 May 2007
Date of preparation: June 29 2007

Start date of project: 1 June 2004
Duration: 31 May 2008

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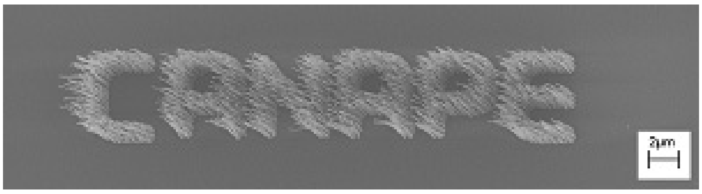
1. Publishable Executive Summary



1.1 Introduction

The CANAPE project aims to deliver some realistic applications of carbon nanotubes. A number of applications are covered, to minimise the risk. Overall, all the deliverables and milestones for year 2 have been met.

The project is organised into 7 technical work packages and 2 other work packages. WP1 is the growth of carbon nanotubes by chemical vapour deposition and the scale-up of production. WP2 is the use of nanotubes and nanostructured carbon as a catalyst in large-scale chemical reactions such as the dehydrogenation of ethyl benzene to styrene. WP3 concerns electronics, and the development of carbon nanotubes for use as metallic interconnects in future integrated circuits, field effect transistors in future integrated circuits, and for field emission-based electron guns in vacuum microelectronics and microwave power amplifiers for satellite base stations. WP4 involves the use of carbon nanotubes in polymer composites, for improved mechanical stiffness or toughness, electrical conductivity, thermal conductivity and in potential aerospace applications. WP5 involves the use of carbon nanotubes being ordered and manipulated by techniques found in surface chemistry and biology, for use as bio-sensors. WP6 measures the toxicological effects of carbon nanotubes, fullerenes and nanostructured forms of carbon, to assess possible health risks. WP7 develops the use of carbon nanotubes as catalyst supports and means to improve the electrode efficiency in polymer membrane fuel cells. There are 2 other work packages, WP8 on training and outreach, and WP9 on management.

1.2 Partners

Participant. Role	Participant. Number	Participant name	Participant short name	Country	Date enter project	Date exit project
CO	1	Cambridge University	Cam	UK	1	48
CR	2	Thomas Swan	Swan	UK	1	48
CR	3	Hitachi Europe Ltd	Hitachi	UK	1	48
CR	4	Max Planck Institute	MPI	D	1	48
CR	5	MPI-Fritz Haber Institute	FHI	D	1	48
CR	6	left				
CR	7	Technical University Darmstadt	TUD	D	1	48
CR	8	University Montpellier II	Mon	F	1	48

CR	9	CRIF	CRIF	B	1	48
CR	10	EMPA	EMPA	CH	1	48
CR	11	CNR Bologna	CNR	I	1	48
CR	12	ST Microelectronics	ST	I	1	48
CR	13	Imperial College, London	IC	UK	1	48
CR	14	Centre Spatial de Liege	CSL	B	1	48
CR	15	Thales	Th	F	1	48

1.3 Coordinator contact details

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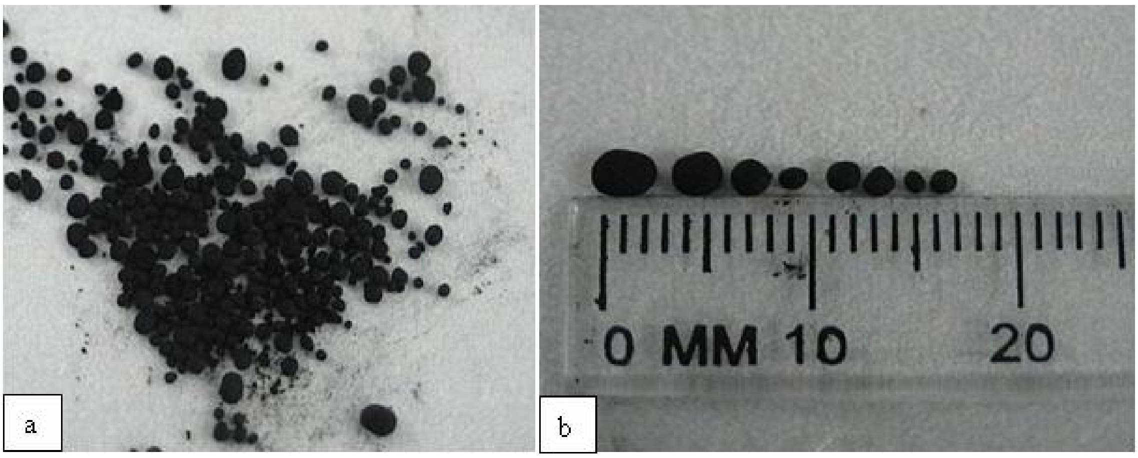
1.4 Objectives

- To scale up the chemical vapour deposition of single-walled and multi-walled carbon nanotubes towards a level of 1 ton/year.
- Develop and scale-up the use of herringbone multi-walled carbon nanotubes to catalyse the oxidative dehydrogenation of ethyl benzene to styrene, reducing temperature by 100C from existing process.
- Develop techniques for the lateral growth of carbon nanotubes at defined positions, for use as components in electronic devices, as interconnects, and vias.
- Reduce nanotube contact resistance to 100Ω, by paralleling if necessary, for interconnects in integrated circuits
- Make spin-polarised contacts to nanotubes to study spin coherent transport for possible future quantum computers.
- To develop a nanotube field effect transistor of high transconductance for the post-CMOS era.
- To develop patterning and orientation techniques for nanotubes using microfluidics and rheology to below 5 μm scale by printing.
- To develop localised vertical growth of CNT of 15 nm diameter. To fabricate high brightness CNT electron sources of 5A/cm^2 for microwave-triodes.
- Develop nanotube-polymer composites of high nanotube loading, with high stiffness, high thermal conductivity, and high electrical conductivity, by control of the alignment, functionalization, loading and inter-linking of nanotubes and the polymer host.
- Develop improved catalysts for polymer membrane fuel cells with higher power densities of 500mW/cm^2 by improved electrical, ionic and gas contact.
- To functionalise nanotubes with biologically active molecules, proteins and receptor units to develop prototype systems for sensors.
- To gain data on possible toxicity of nanotubes by in-vitro tests, advise of safe use, and carry out a public acceptability program.
- To hold annual open workshops and training, to train students and post-docs in techniques of nanotechnology.

1.5 Summary of major achievements during the reporting period

Two nanotube synthesis methods are being developed for large scale production, the more mature fluidised bed method and the newer vapour phase method. Scale up of nanotube production with the fluidised bed method has proceeded. The production capacity is according to the plan, but demand remains less than production. Thus, the final largest scale plant will not be built yet. On the newer vapour phase catalyst method, the process conditions in terms of temperature, catalyst, reactant ratios and throughput are being optimised. This method is able to produce either single walled or multi-walled nanotubes, depending on the process conditions, particularly the catalyst to reactant ratio.

The development of nanostructured carbon catalysts for novel catalysis is proceeding well. The reaction of most interest is the production of styrene by the oxidative dehydrogenation of ethyl benzene. A range of nanotube based catalysts have been studied on micro-scaled pilot reactors, at the level of 5kg/day. The catalysts included SWNTs, MWNTs, nanofibres, and herringbone tubes from numerous manufacturers. In addition, nanotubes grown on activated carbon host material was studied, as a technical catalyst. Ways to pelletise the catalyst is being studied.



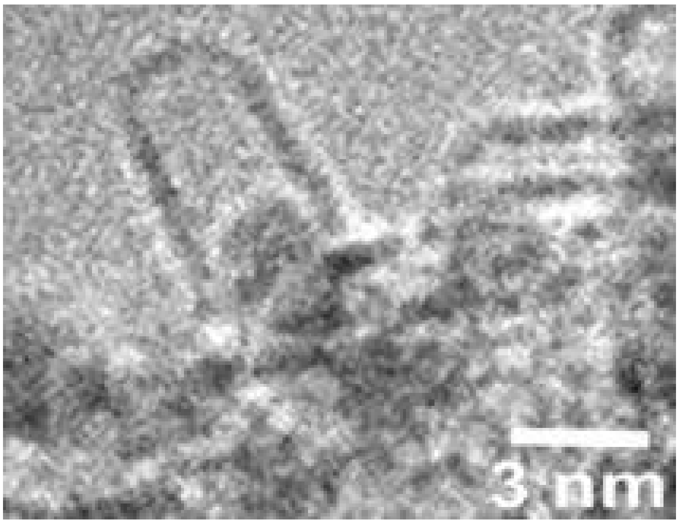
Pelletised catalyst

The most important result of the project this year is the development of a nanotube based catalyst which has comparable production rate and selectivity of styrene (ST) of the existing commercial catalyst of Sud-Chemie. It uses the oxidative dehydrogenation reaction, rather than just a dehydrogenation reaction, so it operates at 200C lower temperature, and with much less energy input (the energy is supplied instead by the oxidation reaction itself).

Catalysts	O_2/EB ratio	Steam/EB ratio	T (^oC)	ST Sel.	ST Yield	Production rate (mmol-ST/g_{cat}.h)
MWCNTs	0.25	0	360	**95.4%**	20.0%	**2.3**
K-Fe (S6-20, BASF)	0	10	550	96.2%	29.2%	1.2
K-Fe (Süd Chemie)	0	12	550	93.9%	72.9%	3.4

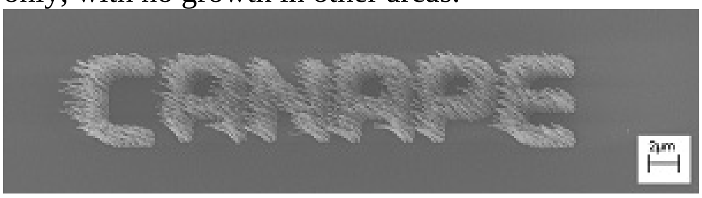
In addition, the overall reaction mechanism on carbon catalysts is becoming more understood. It involves bonding defects on nanotube walls, not graphitic basal planes, as in herringbone nanotubes.

For electronics, Hitachi has applied to patent a growth process for use in their spin valve devices. The spiu valve devices are for use as read heads in magnetic hard disks for computers. In field emission devices, Thales has achieved record modulation of field emission currents at 32 GHz for their microwave amplifiers. This is a considerable achievement. They are also studying possible optical modulation methods of the emission current. In transistors and microelectronics, top gate field effect transistors have been fabricated by direct growth methods. In nanotube growth for microelectronics, Cambridge have achieved an in-situ TEM and XPS study of nanotube nucleation and growth, published in Hofmann et al, Nanoletters **7** 602 (2007). This has enabled the low temperature growth. It also enables future work on vias and interconnects for future CMOS.



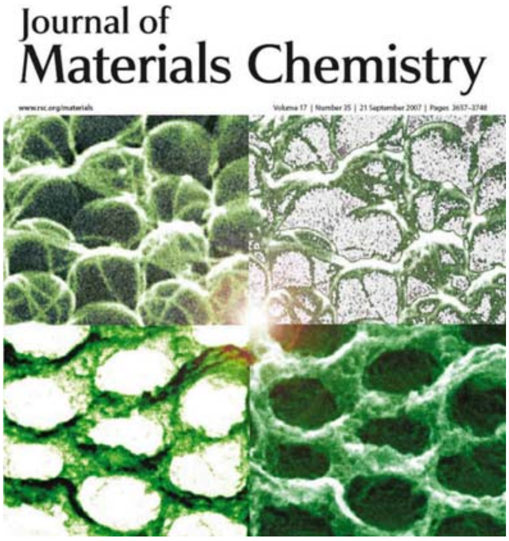
In-situ TEM image of nucleating SWNT.

The Canape logo is an example of controlled nanotube growth. A Ni catalyst was applied by electron beam lithograph onto an oxidised Si wafer, and nanotubes grew on the catalyst areas only, with no growth in other areas.



In composites, heat treatment has been used to improve the wall quality of nanotubes, to be as graphitised, as in carbon fibres. This improves the mechanical properties, which should translate into the mechanical properties of the composites. One of the drawbacks of composites has been that they did not achieve the desired high performance, due to a lack bonding at functionalization. This functionalization is now being studied by Montpellier University by synchrotron radiation measurements using EXAFS, in which the change in electronic density of states due to new bond formation is measured. For conducting composites, electromagnetic shielding attenuation has been measured as 45 dB. Two patents have been applied for by MPI in the important area of transparent conducting composites. For thermally conducting composites, a thermal conductivity of 6.8 W/m.K has been achieved. This is a significant achievement, a deliverable, which makes likely the use of nanotubes as an aerospace component.

Work package 5 has demonstrated the ability to make arrays and electronic devices based on functionalization of nanotubes by biologically active molecule, with the aim of making sensors. The work was used as a front cover image on Journal of Materials Chemistry, 21 Sept 2007 (RSC publications).



The work on fuel cells has met deliverables. Pt-Ru type catalyst nanoparticles have been attached to nanotubes as supports. Preliminary membrane electrode assemblies have been made and load tests carried out. They achieve high enough current densities for the hydrogen usage. Methanol usage will be tested in year 4.

Successful public workshops on Carbon nanotubes were held at FHI, Berlin in October 2006, and a second workshop on Toxicity effects of nanotubes was held in Rome in April 2007. The Berlin meeting was free to the public, and attracted 55 attendees. The Rome meeting had 45 attendees.