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PARNASS

Parallel Nanoassembling Directed by Short-range Field Forces

STRP

SIXTH FRAMEWORK PROGRAMME

PRIORITY 3 - NMP

Nanotechnologies and Nanosciences, Knowledge-based Multifunctional Materials and New Production Processes and Devices

Publishable Executive Summary

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Project coordinator organization name: Fraunhofer IFF

The PARNASS project is intended to bridge the gap between nanoscience and technology by taking recent advances in the underlying physics and chemistry of nanoscale structures and transferring them to the real world of manufacturing engineering and mass production.

Nanoscale structures are usually manufactured either by chemical processes, e.g. by gas phase deposition, by ion or electron beam supported patterning or by the systematic manipulation of individual objects with scanning probe microscopes. The products of chemical processes always exhibit a stochastic distribution, making them suitable for many applications and even advantageous, e.g. nanoscale surface coatings. However, this method cannot be used to manufacture more complex structures consisting of several elements in a functional arrangement. To a certain extent, the latter two methods mentioned can do so but a serial approach is highly ineffective and relatively unsuited for a production process.

Self organization concepts represent one method to effectively manufacture complex nanostructures. In principle, just as gravitation or spring force are expediently used for macroscopic assembly tasks, forces acting on a scale of a few nanometers can be taken advantage of to support assembly operations. On a scale up to approximately 100 nm, electromagnetic fields and thermodynamic effects cause different types of forces to act between objects of the same order of magnitude. The range and effect of these forces differ fundamentally from the known macroscopic effects and their nature and interaction have scarcely been researched so far.

Applying these forces to self-organizing and parallel nanoscale assembly requires fundamentally and thoroughly understanding the mechanisms. This is the objective of the project PARNASS (parallel nanoassembly directed by short-range field forces). Researchers at the Swedish Universities of Halmstadt and Lund, the Spanish University of Taragona, the German University of Leipzig and the Fraunhofer Institute IFF in Magdeburg as well as a manufacturer of ion beam equipment, Raith GmbH in Dortmund are conducting theoretical and experimental analyses of the interaction between various nanoparticles and substrates and developing special tools for analysis and manufacturing. The question of how the skilful selection, chemical modification and mechanical structuring of nanoparticles and substrate can facilitate self-organizing assembly processes is a priority. If the envisioned approach functions successfully, it will, for example, be possible to use established technologies to manufacture highly selective, extremely sensitive chemical sensors able to detecting single molecules cost effectively and in large quantities.

The proof of concept will be delivered at the end of the project. Among other things, this will include lab prototypes of sensors manufactured by the self-organizing assembly of functionalized carbon nanotubes or carbon nanowires on a specially structured substrate that will be able to selectively detect proteins such as antibodies.

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The PARNASS project explicitly concentrates on self-assembly, i.e. on construction processes that control themselves. A similar effect in the macroscopic world is familiar. Gravity or spring forces are used in conjunction with intricate constructions to self-align parts to be assembled. Analogously, nanoscale objects can be placed in environments where they have no other option than to align and behave as desired. Nonetheless, microscopic and macroscopic objects and fabrication have completely different underlying physical effects.

Nanoscale self-assembly is driven by forces that bind nanoscale objects to each other, to surfaces and other nearby structures. Instead of gravity, which is the dominant force for human scale interactions, the acting nanoscale forces are those that give molecules and crystals their shapes and characteristics. They include familiar electrostatic and magnetic forces as well as the van der Waals attraction, i.e. the capillary forces of liquid surfaces, and such forces as the quantum mechanical Casimir force that have been largely ignored for macroscopic objects.

Detailed understanding of nanoscale assembly must be based on sound knowledge of the forces acting on nanoscale objects. This is the fundamental scientific goal of the project, which combines theoretical investigations with sophisticated physical experiments and engineering to create and characterize self-assembled nanostructures.

Casimir and van der Waals forces represent a fast developing, fascinating and important field of science. The intensifying technological interest in this topic in recent years is clearly related to the progress in nanotechnology dominated by the Casimir and the closely related van der Waals forces. Work on theoretical physics in the PARNASS project has focused on better understanding the nature of the Casimir forces and their relation to the vacuum of quantum field theory together with.

Detailed investigations have focused on the role of material properties on these forces and on the validation of theoretical models. Major progress was achieved in the investigation of the dependence of the Casimir force on the geometry of interacting bodies. The divergent nature of the Casimir forces makes such calculations difficult and methods allowing progress in this field only recently became available. In the project, an analytical result was obtained for the first time for a geometry relevant to the real nanoscale objects. Moreover, corrections to the proximity force approximation were obtained for the first time as well, specifically for the geometry of a cylinder and for a sphere in front of plane. This method will be qualified and applied to other relevant setups as the project continues.

Work was also done on directly combining theoretical and experimental approaches to the forces acting between nanoscale object and a substrate at closest distances. A new method, the *method of most bent state*, derived from measurements taken by one of the project partners, delivered quantitative information on these forces. Inspired by these results, a new model for the interpretation of the ultraviolet divergences was developed, which may shed new light on the old problem of the Casimir effect for a conducting sphere. Thus, the work in the PARNASS project has opened a door to new insights into the properties of nanoscale objects and on some other fundamental aspects as well.

Two kinds of nanoobjects are being considered as potential building blocks: semiconductor nanowires and carbon nanotubes. Nanowires are very thin needles of semiconductor material that can be grown on suitable surfaces, standing like a crop of wheat. They can be grown in the place of dedicated assembly or harvested to be placed on other substrates where the self-assembly will be performed. Carbon nanotubes are formed by a graphite sheet that has rolled itself up to create a carbon pipe in which a single or multiple layers of carbon surround an empty central core. The tubes with a single layer of carbon forming the wall have proven to be especially suitable for the fabrication of nanoscale devices. They can be "functionalized" by adding further molecules to the exterior of the tube, which then react with the tube's environment in predetermined ways. In some cases, this reaction changes the tube's electrical conductivity so that a suitable electrical measurement gives a highly sensitive and highly specific method to detect chemical substances.

Three tasks are intended to lead to a quantitative understanding of the forces acting on nanoparticles and the nanoparticles' response to these forces:

- First, preparation techniques will be developed so that suitable substrates can be produced and nanoparticles deposited on them.
- Second, the forces on the nanoparticles will be analyzed qualitatively.
- Finally, qualitative data will be drawn on to derive a quantitative model that can describe and predict the behavior of nanoparticles when acted on by externally engineered force fields.

The consortium institutions applied their research expertise to achieve the first goal rather quickly and had settled on suitable sample preparation and handling techniques for both carbon nanotubes and semiconducting nanowires by the end of the first year. However, as qualitative understanding of the forces acting on typical nanoparticles accumulated, it rapidly became apparent that the partners had underestimated the degree to which friction dominates the movement and interaction of nanoparticles on surfaces and they would have to understand and learn how to control frictional forces before self-assembly could be directed.

The practical measurements were taken by moving the particles with an atomic force microscope (AFM) and measuring their response to various forces. When pushed across the surface by the stylus probe that is the working heart of the AFM, the nanotubes and nanowires adopted shapes that represented a balance between the bending forces imposed by exterior interactions and restoring forces created by the desire to minimize internal stresses. A comparison of the shapes adopted by nanoparticles when they slide across a featureless surface with those that occurred when other nanoparticles or lithographically defined nanopositioners were present revealed that the nanoparticles' interaction with the substrate, i.e. friction, is dominant.

Therefore, a program of experiments aimed at understanding, reducing and eventually controlling friction was commenced. By analyzing the curvature of the particles the partners have been able to quantitatively measure the frictional force between them and their substrate. By studying friction on various substrates, including a hydrophobic surface on which the chemical and physical effects of an adsorbed water layer could be eliminated, the partners have likewise been able to map out general modes of behavior. For example, InAs nanowires below a certain critical size no longer slide smoothly on any substrate but instead move with a jittery, slip-stick motion with a dramatically higher coefficient of friction.

The next step will be to apply the acquired knowledge to the project's chief objective of self-assembly. The goal is to pattern a substrate so that different regions have different degrees of friction. Nanoparticles will then presumably slide across the low friction areas of the surface and attach wherever the friction is higher. Thus the partners will have transformed friction from a problem into at least part of the solution.

The Fraunhofer Institute for Factory Operation and Automation in Magdeburg and Raith GmbH, Dortmund (Germany) are exploring methods to turn the basic science described above into a dependable commercial technology. One specific objective of the project is to design and construct an automated analyzer to investigate the aforementioned fundamental forces. This would give future nanotechnologists a powerful tool to characterize the forces important for their target nanoobjects and to design the self-assembly processes.

The objective of the Fraunhofer IFF and Raith work package is to develop an automated tool for investigations of the interaction forces between nanoparticles and surfaces as well as between the nanoparticles themselves. The nano force analyzer is based on the well established atomic force microscope (AFM) technique and uses special cantilevers optimized for the intended applications. The device can be employed for a variety of applications:

- Force measurements: Specially developed cantilevers allow measurements of the interaction forces between nanoparticles and the supporting substrate as well as interaction forces between the nanoparticles themselves. The outcome is expected to be a precision far superior to existing techniques based on AFM.
- Geometry measurements: Surface imaging and extended metrology can be employed to investigate the physical dimensions of nanoparticles. The lateral resolution of the AFM based metrology measurements is expected to be in the range of 10 nm, whereas the vertical resolution will be less than 1 nm.
- Nanofabrication facility: The analyzer will also provide the capability to fabricate and modify nanostructures. In this case, the AFM tip can be utilized as a nanomanipulator that interacts with the sample surface.

A combination of two commonly used techniques such as SPM and SEM or FIB opens a wide range of opportunities. Integrating SPM/SEM/FIB in a single device constitutes more than merely a combination of complementary microscopy techniques. SPM probes can not only be used as sensors but also as cutters, task tools or end effectors to process surface sample. They can also be used to manipulate individual nanoscale objects and assemble them in required configurations. Generally speaking, such an integrated device could be used for more than precision measurements of static short-range forces and may have much broader application for the design, production and analysis of nanostructured surfaces, which is one of the project's specific objectives.

Automating the whole system, the core element of an integrated device would be a special automatic tool changer with high positioning accuracy. The "tool" could be any means to either characterize or modify surface samples, including nanoparticle manipulation. The main purpose of the changer is to position the requisite tool and its sensing or effecting element where desired and, when necessary, replace it automatically with another tool with the requisite alignment accuracy and repeatability.

The use of modern SEM or FIB microscopes as hosting systems presents a major problem. Their vacuum chambers provide practically no free space since they typically are already equipped with a number of densely packed modules and units such as integrated gas injectors for beam-induced deposition and etching, X-ray analyzers and other analytical detectors. Additional space is not available for manipulators or feed mechanisms with magazines to exchange task tools or processing tools, which are commonly used in automated machines such as CNC.

The partners determined that a "turret-like" automatic tool changer solves this problem optimally. In such a changer, task tools or processing tools (probes or grippers) or their holders are mounted on the rotary support, the fulcrum of which is offset relative to the optical axis of the SEM. This solution has two main advantages:

- Compact design: A smaller mechanical loop eliminates external low frequency mechanical noise and lowers the amount of thermal drift.
- Existence of a geometric locus curve: The SEM can be focused and force-probe placed consistently on the geometric locus curve, thus ensuring the requisite accuracy when replacement tools are positioned and aligned. It is sufficient to position and align tools so that their sensing or effecting portions touch on the locus curve.

The main challenges when designing the "turret-like" automatic tool changer were:

- Devising and engineering proper kinematics and a self-seating tool holder design;
- Designing an appropriate self-seating rotary support with the means to align and adjust it; and
- Fabricating all parts to conform with ambient conditions and electromagnetic considerations in order to prevent SEM image disturbances and vacuum deterioration.

The prototype nano force analyzer was engineered, built and tested with emphasis on its accuracy and repeatability. A novel approach to kinematically mounting precision SPM components was developed and implemented. The novel designs of the automatic probe changer and self-seating tool holder enables positioning probes with great accuracy and reproducibility. Moreover, the compact design creates a smaller mechanical loop, thus eliminating external low frequency mechanical noise and reducing the amount of thermal drift. The general functionality was evaluated and the imaging capability of the combined SPM and SEM in concerted action was demonstrated. The analyzer is expected to have an impact beyond the confines of the research project, for instance, as a future nanoengineering option in standard e_LiNE systems.

<u>Project partners from University Rovira i Virgili</u> in Tarrgona researched the basic chemistry and processing needed to functionalize carbon nanotubes for use. Taking single-walled carbon nanotubes (SWCNT) as the basis, a sensing device was developed in the form of a carbon nanotubes field effect transistor (CNTFET).

Since their discovery in 1991, carbon nanotubes (CNT) have been used for many purposes because of their outstanding properties. The electrical properties of SWCNT make them useful as the semiconductor channel, i.e. the transducing element, in FET. Moreover, although carbon nanotubes are extremely rugged and inert structures chemically, their electrical properties are highly sensitive to charge transfer and the effects of chemical doping by different molecules.

Carbon nanotubes are surrounded by a cloud of π-electrons. Species in the environment can discharge or absorb electrons (hence changing the measurable electrical current passing through the carbon nanotube if two electrodes are placed in both cap ends of a carbon nanotube). A carbon nanotube in air is called a p-type semiconductor because oxygen absorbs the π-electrons and the electronic positive holes determine the intensity through the carbon nanotube. If NO_2 were introduced instead of O_2, the intensity would increase because NO_2 has a greater affinity for electrons than O_2 and thus the number of positive holes would increase. If NH_3 were introduced, the intensity would decrease because NH_3 adds electrons to the cloud of π-electrons.

The intensity of the current passing through a carbon nanotube is quite low (microamperes or nanoamperes). This suggests they could be used (with current amplification devices) to detect of small amounts of analyte. Unfortunately, this sensitivity is connected with very low selectivity, i.e. virtually any analyte that can discharge or absorb electrons is able to change the conductivity of SWCNT. This necessitates functionalizing carbon nanotubes to make them selective for the target analyte. Such selectivity can be achieved by attaching a receptor molecule to the SWCNT, which selectively binds to the target analyte.

The presence of ligands (target analytes to be detected in the test samples) bound to the receptor molecules induces changes in the electrical conduction of the SWCNT, thus providing the mechanism to detect and transduce the electrical signal. Usually, a polymer film is also needed to coat the gaps in the surface of the SWCNT where no molecular receptor has been attached in order to prevent interaction (and charge transfer) between the surface of SWCNT and interference in the surrounding environment.

Therefore, CNTFET consists of the following components:

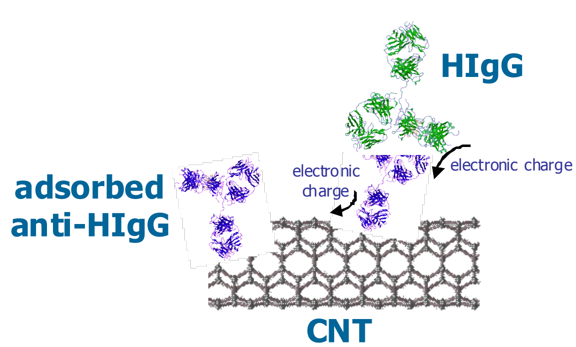
- Transducer: single-walled carbon nanotubes (SWCNTs) that act as the semiconductor channel bridging the source and drain electrodes. The measured intensity between the source and drain electrodes for a fixed source-drain potential (Vsd) can be modified by the potential applied to the gate electrode (Vg).
- Sensor: a suitable molecular receptor able to selectively interact with the selected target analyte and transfer an electronic charge to the single-walled carbon nanotubes.

The selection of the suitable molecular receptor depends on the target analyte selected for detection. Several options open for specific applications of this kind of sensor depending on the receptor being used and the target analyte to be detected. Two applications are the detection of:

- Antigens (e.g. human immunoglobulin G-HlgG) by using antibodies (e.g. anti-HIgG)
- SO_2 by using Pt (II) aryl complex receptors.

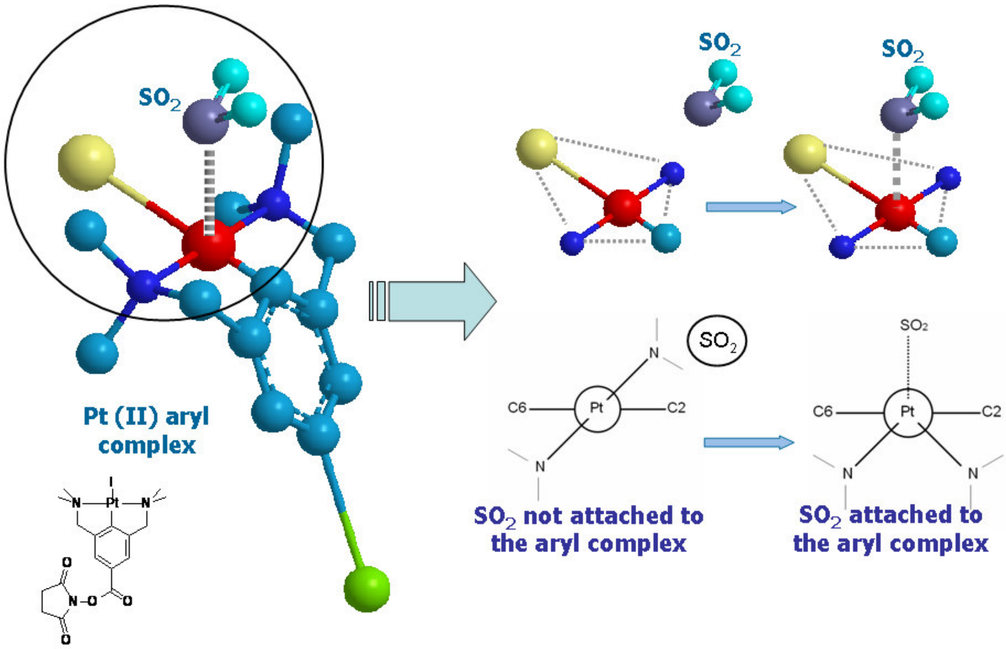
The sensory device developed and first device prototypes built served as the basis for developing complete schemes for the functionalization of CNTFET to detect of nanomolar concentrations of human immunoglobulin G (HIgG) and airborne concentrations of SO_2 below 0.3%.

HIgG is detected based on the change in the intensity of the flow through the CNT due to interaction between anti-HIgG and HIgG:



With this strategy, on-line measurements can detect nanomolar concentrations of HIgG even in the presence of interfering substances such as bovine serum albumin (BSA), the most plentiful protein in blood.

SO_2 can be detected in the gaseous phase when it interacts with the Pt (II) aryl complex, which complexly selectively reacts with SO_2:



With this sensing molecule, the partners have been able so far to detect 0.3% of SO_2 in the gaseous phase even in the presence of interfering gases such as CO_2.

Finally, at the end of the project, the combination of top-down technological approach and bottom-up basic science approach shall result in a proof-of-concept technology where the whole expertise of the partnership leads to creation of self-assembled nano-devices, which can be potentially manufactured in large numbers.