



NANOYOU Teachers Training Kit in Nanoscience and Nanotechnologies

Chapter 7 – Fabrication Methods

Module 1- Fundamental concepts in nanoscience and nanotechnologies

Written by Luisa Filipponi and Duncan Sutherland Interdisciplinary Nanoscience Centre (iNANO) Aarhus University, Denmark January 2010

Creative Commons Attribution ShareAlike 3.0 unless indicated in text or figure captions.

This document has been created in the context of the NANOYOU project (WP4). All information is provided "as is" and no guarantee or warranty is given that the information is fit for any particular purpose. The user thereof uses the information at its sole risk and liability. The document reflects solely the views of its authors. The European Commission is not liable for any use that may be made of the information contained therein.





Contents

Page **2** of **21**





Chapter 7: Fabrication methods

This chapter summarises some of the methods used for the fabrication of nanomaterials, meaning materials with at least one dimension in the nanoscale regime (1-100nm). These include nanostructured surfaces, nanoparticles, nanoporous materials, etc. The aim of this chapter is to answer the questions: how do we fabricate nanomaterials? What fabrication tools are used in nanoscience and nanotechnologies?

Methods for fabricating nanomaterials can be generally subdivided into two groups: **top-down** methods, and **bottom-up** methods. In the first case nanomaterials are derived from a bulk substrate and obtained by progressive removal of material, until the desired nanomaterial is obtained. A simple way to illustrate a top-down method is to think of carving a statue out of a large block of marble. Printing methods also belong to this category. **Bottom-up** methods work in the opposite direction: the nanomaterial, such as a nanocoating, is obtained starting from the atomic or molecular precursors and gradually assembling it until the desired structure is formed. The method resembles building with Lego® bricks.

In both methods two requisites are fundamental: control of the fabrication conditions (e.g. energy of the electron beam) and control of the environment conditions (presence of dust, contaminants, etc). For these reasons, nanotechnologies use highly sophisticated fabrication tools that are mostly operated in a vacuum in clean-room laboratories.

Top-down

Numerous top-down fabrication methods used in nanotechnologies are derived from the fabrication methods used in the semiconductor industry to fabricate the various elements of computer chips (integrated circuits). These methods are collectively called **lithography** and use a light or electron beam to selectively remove micron-scale structures from a precursor material called **resist**. In recent years there has been a tremendous push to reduce the size of electronic devices and integrate more functions into them, which has been possible thanks to the advances in lithographic fabrication methods. Page **3** of **21**





Nowadays it is possible to obtain single features below 100nm (the transistors in latest generation processors are about 45 nm). **Therefore in the semiconductor industry nanostructures are routinely fabricated**. Lithographic methods that are capable of producing nanoscale features are reviewed in the next section.

There are many more methods to fabricate nanostructures top-down; here we limit the discussion to the most common ones.

Conventional lithography

Lithography includes a series of fabrication techniques that share the principle of **transferring an image from a mask to a receiving substrate**. A typical lithographic process consists of three successive steps: (i) coating a substrate (Si wafer or glass) with a sensitive polymer layer (called resist), (ii) exposing the resist to light, electrons or ion beams, (iii) developing the resist image with a suitable chemical (developer), which reveals a positive or negative image on the substrate depending on the type of resist used (i.e. positive tone or negative tone resist). In conventional microfabrication used in the semiconductor industry, the next step after lithography is the pattern transfer from the resist to the underlying substrate. This is achieved through a number of transfer techniques, such as chemical etching and dry plasma etching.

Lithographic techniques can be broadly divided in two main groups:

1. Methods that use a **physical mask**, where the resist is irradiated through the mask which is in contact or in proximity with the resist surface. These methods are collectively called mask lithography, among which photolithography is the most used.

2. Methods that use **software mask**. Here, a scanning beam irradiates the surface of the resist sequentially, point by point, through a computer-controlled program where the mask pattern is defined. These methods are collectively called scanning lithography.

The main difference between mask and scanning lithography is speed: whereas mask lithography is a parallel, fast technique, scanning lithography is a slow, serial technique. Another important difference is resolution which, in general terms, is higher for scanning methods. The price paid for higher resolution is the use of more energetic radiation sources, which entails expensive equipment.

Page **4** of **21**



Photolithography

Photolithography uses light (UV, deep-UV, extreme-UV or X-ray) to expose a layer of **radiation-sensitive polymer** (photoresist) through a mask. The mask is a nearly optically flat glass (or quartz, depending on the light used) plate which contains the desired pattern: opaque areas (the pattern, made of an absorber metal) on a UV-transparent background. The image on the mask can be either replicated as it is, placing the mask in physical contact with the resist (contact mode photolithography) or reduced, usually by a factor of 5 or 10, and projected to the resist layer through an optical system (projection mode photolithography).



Figure 1. Conventional use of photolithography in the semiconductor industry for fabricating elements in integrated circuits (e.g. computer chips). A photoresist is deposited on a silicon wafer, exposed to light through a mask, and the exposed area selectively removed with a developer. The resulting pattern can be used as a "mask" for chemical etching, or as a pattern where a metal is selectively deposited. (Image credit: L. Filipponi, PhD Thesis: "New micropatterning techniques for the spatial immobilization of proteins" (2006), Copyright L. Filipponi, Creative Commons Attribution ShareAlike 3.0)

The resolution of contact mode lithography is typically 0.5-0.8 μ m when UV light (360-460 nm) is used. Higher resolutions cannot be achieved due to the inability to reduce the gap between the mask and the Page 5 of 21





flat substrate below ~1µm, even when elaborate vacuum systems are used to hold the two parts together. To produce patterns with higher resolution, projection photolithography or "next-generation photolithography" techniques (i.e. extreme UV and X-ray photolithography) need to be employed. These technologies use very expensive equipment and therefore their use is limited to selected applications (such as photomask fabrication). The equipment needed is available only in specialised laboratories.

Scanning lithography

Energetic particles such as **electrons and ions can be used to pattern appropriate resist films** leading to features with nanometre resolution. When using electrons, the technology is called electron beam lithography (**e-beam**), whereas when using ions the technology is called **focused ion beam lithography**. Finally, a recently established technology uses nanometre scanning probes for patterning resist films and is therefore referred to as scanning probe lithography (SPL). This technology has been extended to the deposition of nano-quantity of material (Dip-pen nanolithography, DPN).

E-beam lithography

In a typical e-beam lithography process, a tightly focused beam of electrons scans across the surface of an electron-sensitive resist film, such as poly(methyl methacrylate) (PMMA). The main advantage of e-beam lithography over photolithography is its high resolution: patterns with **features as small as 50 nm** can be routinely generated. The resolution of this technology is mainly determined by the scattering of the electrons in the resist film and the substrate. When using particles with a mass higher than electrons, however, this effect is largely reduced. Focused ion beam lithography works on the same principle of e-beam lithography, but ions such as H⁺, He⁺⁺, Li⁺ and Be⁺⁺ are used. Both techniques provide a resolution much higher than photolithography but share a main disadvantage: both are serial techniques, very slow in process, so their use is mostly limited to producing photomasks in optical lithography.

Soft lithography

Soft lithography is a name for a number of techniques that fabricate and use a soft mould prepared by casting a liquid polymer precursor against a rigid master. These methods have been **developed specifically for making large-scale micro and nanostructures with equipment that is easier to operate compared to those used in "conventional" lithography**, cheaper and also available in biological laboratories. **Figure 2** shows the overall principle of soft lithography.

Page 6 of 21







Figure 2. Overview of a soft-lithography replication process. A silicon master is replicated with PDMS. The pre-polymer is poured (it is a very viscous liquid) over the master, cured at 65°C for 2 hours (temperature and curing time can be adjusted). The polymer solidifies but remains very flexible. The PDMS mould is peeled off from the master, and a negative copy obtained. AFM images of the master and the PDMS replica are in Figure 3. (Image credit: from L. Filipponi, PhD Thesis: :"New micropatterning techniques for the spatial immobilization of proteins" (2006), Copyright L. Filipponi, Creative Commons Attribution ShareAlike 3.0)



Figure 3. An AFM image of an array of pyramidal wells in a silicon master (left) and pyramidal posts in a PDMS replica (right) imaged with AFM. (Image credit: from L. Filipponi, PhD Thesis: :"New micropatterning techniques for the spatial immobilization of proteins" (2006), Copyright L. Filipponi, Creative Commons Attribution ShareAlike 3.0)

Page **7** of **21**





The resolution of soft lithography is mainly determined by van der Waals interactions, by wetting and by kinetic factors such as filling the capillaries on the surface of the master, but not by optical diffraction. This is an important advantage over "conventional" lithographic techniques. The master is normally fabricated via a conventional lithographic method.

Various polymers (e.g. polyurethanes, epoxides and polyimides) can be used for moulding; most commonly, the elastomer poly(dimethylsiloxane) (PDMS) is used. PDMS is non-toxic so it can be used safely with biological materials, including live cells. This is a big advantage in devices that aim to integrate nanostructures with biological systems.

A PDMS mould is fabricated by pouring its liquid precursor over a lithographically-made master (e.g. a photoresist or silicon master), cured to induce cross-linking, and then peeled off from it. The stamp can then be used either for printing a desired material (the "ink") from the stamp to a suitable surface (microcontact printing, μ CP) or, when in contact with a flat or curved surface, to define physical constraints where a liquid can be confined.

Nanocontact printing

Microcontact printing is useful for patterning features with lateral dimension of 500nm or larger. One of the major challenges for μ CP has been to achieve the capability to print with high resolution, i.e. with **lateral dimension lower than 100 nm**. This has been recently achieved by improving the stability of the PDMS, which, being soft and highly compressible, has a tendency to deform and collapse. One way to improve the stability of the patterns is to affix a stiff backplane to the stamp or to change the chemical formulation of the stamp itself, in order to obtain a harder polymer. With these modifications, it is now possible to print features as small as 50 nm. This printing method, which uses harder stamps, is called nanocontact printing (nCP).

Nano-imprint lithography

The concept of nano-imprint lithography is to use a hard master with a 3D nanostructure to mould another material, which assumes its reverse 3D structure. Imagine taking a Lego[®] block and pressing hard on a piece of play dough. Since the master has a fine nano-structure, to be successful the process must be done under pressure, a coating must first be placed on the master to avoid catastrophic adhesion to the mould, and the mould must be heated (above its Tg temperature) in order to be soft

Page **8** of **21**





enough to completely enter the fine master nanostructure and be effectively replicated. The method is the equivalent of embossing at the nanoscale. It requires specialised equipment.

Nanosphere lithography

In nanosphere lithography an ensemble of nanospheres ordered on a surface are used as a mask. The nanospheres are dispersed in a liquid (i.e. a colloid) and a droplet placed on a surface and left to dry. Depending on the surface properties (e.g. charge) and media used in the colloid (e.g. presence of electrolytes) the nanosphere will self-assemble in an ordered pattern. In some conditions, a colloidal crystal is obtained: each nanoparticle is surrounded by six other nanospheres. This regular arrangement (which is a **2D colloidal crystal**) can be used to create ordered structures on surfaces.

TIP TO TEACHER: To illustrate this in class, take a number of spherical beads and pour them onto a shallow plate. The beads will self-organise in the same way.

In the regular arrangement of nanospheres there will be an empty space between them, which is regularly repeated in the entire surface. In the most simple method, this space is employed to create relatively flat nanopatterns on the surface. The nanosphere pattern is used as a mask, and a material (e.g. gold, silver, etc) sputtered on top of it. Once the nanospheres are removed, a regular pattern is left of "dots" each shaped like a triangle but with concave sides.



Figure 4. Nanosphere lithography. SEM images of a latex nanosphere mask ($2 \mu m SiO_2$ beads) (left) and triangular gold nanoprisms (right) obtained by evaporating gold over the colloidal mask (nanosphere lithography). (Image credit: courtesy of R. Ogaki, iNANO, Aarhus University, Copyright 2008).

The gold pattern ("dots") can also act as growth sites, for instance for the growth of carbon nanotubes or ZnO .**The result is a regular array of nanotubes or nanowires**, as shown in **Figure 5**.

Page **9** of **21**





Figure 5. Top and a 30° view of aligned ZnO nanorods, where the hexagonal pattern is apparent. (d) Aligned ZnO nanorods at the edge of the growth pattern. (reprinted with permission from Wang et al. Nano letters (2004), 4(3), pp.423-6. Copyright (2004) American Chemical Society).

Nanosphere lithography has now evolved into a method that allows the fabrication of very complex arrays of nanostructures, including **3D features with small holes in them**.

Colloidal lithography

Colloid lithography shares the same principle of nanosphere lithography of using a colloid as a mask for the fabrication of nanostructures on surfaces. In this method electrostatic forces are employed to obtain short-range ordered arrays of nanospheres on the surface.

The array can then be used to create a number of different nanostructures, through various processes like etching, liftoff, etc.

1000 nm

Etching



Without going into details of the method, what is interesting is to note the different types of nanostructures that can be formed: holes, cones, rings, "sandwiches" made of different materials, etc.

Page **10** of **21**







If made of metals, these nanostructures present a localised surface plasmonic resonance effect (LSPR) which can be used for sensing. These materials are therefore under study for various **sensing applications** (e.g. for medical devices).

Figure 7. Summary of the various nanostructures that can be formed as regular arrays on surfaces. (Image courtesy of D. Sutherland, iNANO; Aarhus University).

Scanning probe lithography

Scanning probe microscopy (i.e. STM, AFM, etc.) uses small (<50 nm) tips to image surfaces with atomic resolution (these methods are described in **Chapter 6 of Module 1 "Characterisation techniques"**). This ability suggests opportunities for their use in generating nanostructures and nanodevices. In this form they are referred to as **"Scanning Probe Lithography" (SPL)**, which uses the tip of an AFM to selectively *remove* certain areas on a surface and **"Dip-pen nanolithography" (DPN)**, which, similarly, uses the AFM tip to *deposit* material on a surface with nanometre resolution.



Figure 8. (Left) The operation principle of DPN. The AFM tip is coated with a liquid containing the molecules to be deposited. As the tip scans the surface, the molecules are deposited through the water meniscus that forms between the tip and the surface. (Image credit: reprinted from "Small science gets to the heart of matter", Science and technology review 2001). (Right) part of the famous speech "There is plenty of the room at the bottom" by Prof. R. P. Feynman written with SPL. (Image credit: C. Mirkin. Northwestern University)

Page **11** of **21**



Both are direct writing techniques and their main advantages are high resolution and the ability to generate patterns with arbitrary geometries. Like e-beam and ion-beam lithography, SPL and DPN are serial techniques whose main limitation is speed.

Writing "atom-by-atom"

A particular feature of an STM is that it can be used for more than just to visualise atoms. Twenty years ago researchers at IBM were able to demonstrate that they could use the STM tip to carefully move atoms on a surface and write the company logo with atoms, as shown in **Figure 9**.



Figure 9. Actual sequence of STM images as reported in the original paper that demonstrated for the first time that writing with the STM is possible. (Reprinted from: Eigler at al., "Positioning single atoms with a scanning tunnelling microscope ", Nature (1999, 5 April), vol. 344. Copyright Nature Publishing Group (1999). Permission requested).

If one were to write using atoms, letters would be around 1 nm each. With letters of this size we could easily write the whole of Encyclopedia Britannica in an area as small as the tip of a human hair (10^{-4} m^2) . Indeed with letters of this size we would get all the world's books to fit on a single A4 sheet, but it would take incredibly long to write, and in addition they could only be read with the STM.

Nevertheless the ability to move individual atoms using an STM has great potential for the future generation of **data storage devices**.

Today, data is stored in CD-ROMs using minute "bits" of semiconductors around 0.1 micrometers (10⁻⁷ m) in size. If these bits were instead written with atoms, we would be able to achieve far greater data capacity. One of these "nano-CDs" with "atomic bits" could contain as much information as 1 million current CD-ROMs.

The STM allows building a material atom by atom independently of its chemistry and physics, as shown in **Figure 10**. This can lead to new materials that most likely have completely new properties. The process is still very slow, since the atoms can be moved only manually, and this must be one atom at a time. Mass production of new nano-materials using this method is thus not yet possible.

Page **12** of **21**







Figure 10. This corral is an artificial structure created from 48 iron atoms (the sharp peaks) on a copper surface. The wave patterns in this scanning tunneling microscope image are formed by copper electrons confined by the iron atoms. (Image credit: D. Eigler, IBM Almaden Research Center, NISE Network, www.nisenet.org, reprinted under NISE network terms and conditions)

Bottom Up

Bottom up methods can be divided into gas-phase and liquid-phase methods. in both cases, the nanomaterial is fabricated through a controlled fabrication route that starts from the single atom or molecules:

- Sas-phase methods: these include plasma arcing and chemical vapour deposition;
- Liquid phase: the most established method is sol-gel synthesis; molecular self-assembly is emerging as a new method.

Plasma arcing

This is the most common method for fabricating nanotubes. The method uses a plasma, which is an ionised gas. A potential difference is placed between two electrodes and the gas in between ionises. A typical arcing device in made of two electrodes and an arc that passes from one electrode to the other. The first electrode (anode) vaporises as electrons are taken from it by the potential difference. For instance a carbon electrode is used to produce carbon nanotubes. This is consumed during the reaction, producing carbon cations. These positively changed ions pass to the other electrode, pick up electrons and are deposited to form nanotubes.

Plasma arcing can also be used to deposit nanolayers on surfaces rather than making new structures. The deposit can be as little as a few atoms in depth (and must be at least 1 nm thick to be considered a nanomaterial). In this sense plasma arcing is complementary to chemical vapour deposition (described below).

Page 13 of 21





Chemical vapour deposition

In this method the material to be deposited is first heated to its gas form and then allowed to deposit as a solid on a surface. The method is normally performed under vacuum. The deposition can be direct or through a chemical reaction so that the material deposited is different from the one volatilised. This process is routinely used to make nanopowders of oxides and carbides of metals if carbon or oxygen are present with the metal. The method can also be used to generate nanopowders of pure metals, although not so easily,.

Chemical vapour deposition is often used to deposit a material on a flat surface. When a surface is exposed to a chemical vapour, the first layer of atoms or molecules that deposit on the surface can act as a template on which material can grow. The structures of these materials are often aligned. During deposition a site for crystallisation may form in the depositional axis (the one perpendicular to the surface to be coated). As a result, aligned structures start to grow vertically. This is therefore an example of self assembly.

Molecular beam epitaxy (MBE)

This is essentially a very sophisticated evaporation method in which molecular beams interact on a heated crystalline substrate under ultra high vacuum (UHV) conditions to produce a single crystal film. MEB makes it possible to fabricate crystals one atomic layer at a time. The growth process is highly controlled to avoid contaminants being introduced during the crystal growth. A range of surface analysis techniques is used to monitor the growth process and ensure purity of the crystal. MBE is presently used in the semiconductor industry, where the performance of the device (e.g. computer chip) depends on precise control of dopants in semiconductors and on the production of extremely thin crystal layers with hyper-abrupt interfaces. MBE is used for the fabrication of numerous important devices such as light-emitting diodes, laser diodes, field effect transistors, read/write heads for computer drives and more.

Page 14 of 21



Sol-gel synthesis

This method is performed in the liquid phase. It is a useful self-assembly process for fabricating nanoparticles as well as nanostructured surfaces and three-dimensional nanostructured materials such as aerogels.

A "sol" is a type of colloid¹ in which a dispersed solid phase is mixed in a homogeneous liquid medium. An example of a naturally occurring sol is blood. As the name suggests, the sol-gel process involves the evolution of networks through the formation of a colloidal suspension (sol) and gelation of the sol to form a network in a continuous liquid phase (gel).

The first stage in the sol-gel process is the synthesis of the colloid. The precursors are normally ions of a metal. Metal alkoxides and alkoxysilanes are the most popular since they react readily with water (hydrolysis). The most widely used alkoxysilanes are tetramethoxysilane (TMOS) and tetraethoxysilane (TEOS) which form silica gels. Alkoxides such as aluminates, titanates and borates are also used, often mixed with TMOS or TEOS. In addition, since alkoxides and water are immiscible, a mutual solvent is used, such as an alcohol.

The sol-gel process involves four steps. First the hydrolysis reaction, in which the -OR group is replaced with an -OH group. The hydrolysis reaction can occur without a catalyst but is more rapid and complete when they are used. As in any hydrolysis reaction the catalyst can be a base (NaOH or NH_3) or an acid (HF or CH_3COOH).

After hydrolysis, the sol starts to condense and polymerise. This leads to a growth of particles which, depending on various conditions such as pH, reach dimensions of a few nanometres. The condensation/polymerisation reaction is quite complex and involves many intermediate products, including cyclic structures. The particles then agglomerate: A network starts to form throughout the liquid medium, resulting in thickening, which forms a gel.

Page **15** of **21**

¹ A colloid is a type of chemical mixture where one substance is dispersed evenly throughout another one but the particles of the dispersed substance are only suspended in the mixture, they are not completely dissolved in it. Generally speaking, a colloid is composed of particles in the range of 10-200nm. The dispersed phase can be solid, liquid or gas and the medium in which it is dispersed (called continuous medium) can also be solid, liquid or gas.

The research leading to these results has received funding from the European Community's Seventh Framework Programme (FP7/2007-2013) under grant agreement n° 233433





All the four steps illustrated above are affected by the initial conditions for the hydrolysis reaction and the condensation/polymerisation. These conditions include pH, temperature and time of reaction, nature of the catalyst, etc.

The sol-gel process is very commonly used to make silica gels. Other type of gels can also be formed; aluminosilicate gels are special because they form tubular structures. One such a product is imogolite which has an external diameter of about 2.5 nm and internal tube diameter of 1.5nm. These types of nanostructures are known to be good adsorbents for anions such as chloride, chlorate, sulphate and phosphates. The imogolite structure can be dissolved away with HF. Therefore these nanostructures can be used for template synthesis: the tube can be filled with atoms and then dissolved away, leaving rows of atoms (2.5 atoms of gold in a row measure 1 nm).

Sol-gel process for making nanostructured surfaces

Figure 11 summarises the different sol-gel processes. To make the most of the large surface area of nanoparticles, the gel can be placed on a surface. This way a greater bulk-area ratio is obtained. Another strategy is to form an aerogel. These are three-dimensional continuous networks of particles with air (or any other gas) trapped at their interstices. Aerogels are characterised by being porous and very light yet able to withstand 100 times their weight.

Page 16 of 21





Figure 11. Schematic overview of different materials that can be obtained through a sol-gel process. (Image courtesy of Lawrence Livermore National Laboratory).

A versatile way to create ordered surface nanostructures is to perform the sol-gel synthesis in a liquid which is itself ordered. Liquid crystals are precisely this: they have a crystalline structure but exist in a liquid (rather than solid) phase. Nanostructured silica with controlled pore size, shape and ordering can be made in this way.

The liquid crystalline casting method described above can also be used to produce **nanostructured metals**. This development is very useful for making nanostructured catalytic surfaces, like platinum or palladium surfaces. Since these metals are very rare and expensive, it is highly advantageous to have surfaces where nearly all metal atoms can take part in the catalytic reaction (being on the surface), and not just surface atoms as in conventional solids.

Page **17** of **21**





Functionalised silica glass surfaces

The sol-gel method also allows the incorporation of organic, inorganic and bio-organic molecules within the silica glass structure. Most organic and inorganic molecules cannot be incorporated (doped) in glass because this is prepared using very high temperature. The sol-gel process occurs at relatively low temperatures (in some cases at RT), so these molecules can be incorporated in the process. This makes it possible for instance to incorporate molecules such as enzymes inside the silica glass. The result is a material that has the advantages of plastics (the product can be made in any form, it can be attached to other materials, etc.) but also many improvements: the glasses are inert, more stable to heat and chemical attack, the entrapped molecules do not leach out, and are protected in their reactivity, and the glasses are transparent.²

Molecular self-assembly

Self-assembly is the "fabrication tool" of Nature: all natural materials, organic and inorganic, are produced through a self-assembly route. In natural biological processes, molecules self-assemble to create complex structures with nanoscale precision. Examples are the formation of the DNA double helix or the formation of the membrane cell from phospholipids. In self-assembly, sub units spontaneously organise and aggregate into stable, well defined structures through **non covalent interaction**. This process is guided by information that is coded into the characteristics of the sub-units and the final structure is reached by equilibrating to the form of the lowest free energy.

TIP TO TEACHER: self-assembly is a concept that can easily be integrated into conventional lessons on genetics or biology. There are various size scales of self-assembly, from the molecular level (from proteins to DNA) to "macro" level (evolution of a foetus into a baby). Basically all natural processes are examples of self-assembly.

Until now we have been fabricating devices starting from the top (a large piece of metal) and carving it down to small pieces. Now scientists are considering and studying ways of building materials truly from the bottom up, mimicking Nature's fabrication strategy. Instead of carving nanostructures out of larger materials (which is the typical top-down approach used to fabricate integrated electronic circuits such as

Page 18 of 21

² If nanoparticles or even smaller molecules are added to the glass it remains transparent since nanoparticles do not scatter light. See Chapter 4 for details on this.

The research leading to these results has received funding from the European Community's Seventh Framework Programme (FP7/2007-2013) under grant agreement n° 233433





micromachining and microlithography), nanostructures could be created bottom-up, from atomic building blocks that self-assemble into larger structures.

It must be noted that this is now possible for extremely small objects. The idea of using a computer-assisted program to actually build a device, such as an electronic circuit, atom-byatom, through a self-assembly program is still a vision, but it is possible to fabricate some very small components of an integrated circuit through a self-assembly process (e.g. a nanowire).

In the laboratory, scientists can make use of this self-organisation of matter as a way of programming the building of novel structures with specific functions. Thus the fabrication process is a molecular recognition directed self-organisation. To do so, they insert specific patterns within the molecules to form organised supermolecules - nanostructures making use of supermolecular chemistry. This can be understood as a lock-and-key self-organisation of matter: scientists can pre-organise a "key" in a molecule for a "lock" of another one, or vice versa. Once in proximity, the two (or more) molecules assemble together: the lock-and-key mechanism serves to bind together the two molecules in a specific geometry. In supermolecular chemistry there are no chemical bonds formed during the self-assembly process: the molecules are held together through metal ion coordination, hydrogen bonding, donoracceptor interactions, van der Waals forces and mediation effects (e.g. solvent). Transition-metalmediated structures are a type of supermolecular structures. In these, metal cations are the cement that holds the molecules (the "bricks") together. The interest in supermolecular structure derives from the fact that these can have properties that are dramatically different from those of its components (e.g. change in electric properties). Another method uses the structural motifs and self-recognition properties of DNA to self-assemble pre-designed nanostructures in a bottom-up approach. This field is called DNA nanotechnology.

Two other important types of supermolecular structures that are created through a self-assembly process are **dendrimes** and **cyclodextrins**.

Page **19** of **21**



Figure 12. Dendrimer with 54 ferrocenes attached. (Image source, Wiki Commons, image for public domain)



Figure 13. Three dimensional model of the chemical structure of beta-cyclodextrin. (Image credit: Wiki Commons, image for public domain)

DNA Nanotechnology

DNA nanotechnology exploits the structural motifs and self-recognition properties of DNA to selfassemble pre-designed nanostructures in a bottom-up approach. 2D and 3D structures have been fabricated using this self-assembly method. Recently, the revolutionary **DNA origami method** was developed to build two-dimensional addressable DNA structures of arbitrary shape that can be used as a platform for arranging nanomaterials with high precision and specificity. Researchers at the Centre for DNA Nanotechnology (Aarhus University) have developed a software package to facilitate the design of DNA origami structures and it was initially applied in the design of the dolphins in the former logo of Aarhus University (**Figure 14**).

Page 20 of 21







Figure 14. The researchers began by cutting a dolphin out of the University of Aarhus logo, after which it was used as a template for designing a dolphin-like DNA structure. After producing this in the laboratory, AFM images were taken of the DNA structure thus formed. In the Aarhus University logo an image of the DNA dolphin is reinserted. (Image credit: Danish National Research Foundation: Centre for DNA Nanotechnology (cDNA) and the Interdisciplinary Nanoscience Centre (iNANO) at Aarhus University. Copyright 2009.

The design program was further applied in the design of a three-dimensional DNA box with dimensions $42 \times 36 \times 36 \text{ nm}^3$ that can be opened by external

"key" signals (Figure 15). The controlled access to the interior compartment of the DNA container opens the way for several interesting applications of the DNA box, for example as a **logic sensor** for multiple sequence signals and for the **controlled release of nano-cargos** with potential applications in the emerging area of nanomedicine.



Figure 15. (Left) Atomic models of DNA boxes with dimensions of 42x36x36 nm3 that are large enough to harbour e.g. a whole ribosome. (Right) A cryo electron microscopy (cryo-EM) reconstruction of the DNA boxes mentioned above. (Image credit: Danish Research National Foundation: Centre for DNA Nanotechnology (cDNA) the and Interdisciplinary Nanoscience Centre (iNANO) at Aarhus University. Copyright 2009).

DNA nanotechnology represents one of the latest developments in nanotechnology. It has applications for the fabrication of nano guides (e.g. wave guides), sensors (for diagnostic and imaging), logic gates, drug release, nano-motors and electronics (wires, transistors). It could lead to bottom-up electronics and DNA computing which could become the computing of the future.

Page **21** of **21**