

Organic bottom up nanostructures:

Nanostructures are supposed to have a high potential for further technologies. As they are difficult to produce, growing is one of the approaches taken to fabricate them with the eventual goal of mass production.

The presentation wants to give a brief overview how growing works in nature taking proteins as an example. Following this it shows some of the current production methods for different kinds of nanostructures.

Organic bottom up nanostructures can be seen like crystal growth with organic substances. The main idea is that on a nanoscopic scale the atoms organize themselves into the desired structure. In order to do so the design has to provide a minimum of energy of the atom/molecule at the expected position. Whitesides et al wanted to introduce growth as a new production method, competing with the existing ones. Taking a look at the size scale this seems to be a useful idea to close the gap between lithography and synthesis. The main problems to do this are the control of the dimensions, the morphology and the monodispersity (or instead of monodispersity the phase purity and chemical composition). Solving these problems will be crucial to succeed in any further attempts to use growth as a production method. Otherwise the problem had to be changed in a way that none of the fields listed above influence the final result. Though mechanical linkages were introduced as an idea for general growth mechanisms, they don't seem to be useful for nanostructures.

Proteins are presented because they are what could be described as a goal. They give many ideas what nanostructures could be used for and also how they eventually could be produced. Proteins are chains of different amino acids that fold themselves into working three dimensional structures. By definition, they are given different names for their different structures. These different structures (primary, secondary, tertiary and quaternary) are introduced. Amino acids, the construction blocks for proteins, are shown in their general shape and in some specific ones. The peptide bonds that link them are activated by other enzymatic proteins, the reaction does not take place without them. Once the protein chain, which was read of DNA, is finished, the protein has to fold. On the way to the folded protein, one distinguishes between the secondary and the tertiary structure. Examples for different secondary structures are given, but the most important ones are the alpha helix and the beta sheet. They fold into what is known as the tertiary structure. The process of folding is still subject of today's research and it is only known that hydrophobicity plays a major role. Though it can be shown how proteins can be disturbed in folding, predicting the structure of a folded protein from its primary structure is very difficult. There are many experiments which confirm that hydrophobic interactions are the driving force in the folding process. But as usually in biophysics, they are not the only driving force and the exact way yet has to be determined. Conclusively, proteins show very good how organic nanostructures could look like. And they do not even use all the possibilities, in example magnetic interactions have not been observed. It is important to point out that unlike grown structures, proteins are assembled molecule by molecule and not by self organization. The folding is the process of self assembly and also the part which can give many clues for other structures. Proteins are polymeres and what makes them unique are the facts that they do not only fold into certain structures but also that these new structures can fulfill tasks.

As a first example for self-assembled nanostructures micelles are shown. They represent the simplest way of self organization, as they are organic structures with one hydrophobic and one hydrophilic side. Thus, in the right concentration, they try to form circles, where the hydrophobic side forms the core and the hydrophilic part is around it facing the water or any other polar solvent. In the presentation, an experiment performed by Spatz et al is described, where the ability of self organization of micelles is used to form a regular array of gold particles. The single steps that were done are to be found in the presentation. The micelles were later on removed with the help of plasma, which unfortunately can also influence the particles.

The gold array may later be used for further growth of nanowires providing an ordered structure for it.

Templating with micelles is another example for their usage. Here, the concentration has to be varied in a way that the micelles form rod like structures. The implanting of any other material remains similar to the first micelle example for the formed gold array. A main problem is the removal of the template, which was performed using a plasma in the first example for micelles. Also, the preparation of the micellar phase may be tedious and difficult.

Growing one-dimensional crystals is a good example for self organized structures. Though the two shown examples are inorganic materials, they give an idea how growing with organic materials works. Molybdenum chalcogenides naturally grow into 1D nanostructures if it is grown from vapor phase. This habit is determined by the highly anisotropic bonding in the crystallographic structure. When dissolved in a highly polar solvent, they mainly exist as chains of about 2 nm in diameter. Some chains might even aggregate into bundles. Growing Selenium crystals by cooling down amorphous dissolved Se is another approach to get nanowires. The trigonal (t-) phase of this solid is interesting because of its rather unique crystal structure. Unlike oxygen, Se atoms tend to form polymeric, helical chains through covalent bonding. The helical chains can be readily packed into a hexagonal lattice through van der Waals interactions. As dictated by this highly anisotropic structure, crystallization tends to occur along the c-axis, favoring the stronger covalent bonds over the relatively weak van der Waals forces among chains. As a result, this solid has a tendency to become a 1D structure even when crystallized from an isotropic medium. This is further supported by the intrinsic chirality, another remarkable phenomena. The resulting bundles demonstrate the main problem of grown nanostructures that prevents them from being used in any production method, as they do not show uniform size or positioning, two crucial issues for every common production method.

Growing structures with organic materials, the presented example being bolaamphiphiles, gives many options about the possible design of nano- and in this case also microstructures. The problem with these structures is that they can be synthesized but not really be understood. By variation of different parameters and attributes of the used bolaamphiphiles the eventual structure can be changed. Yet changes can be only observed, their precise structure cannot be predicted, and the influence of many parameters remains unknown, too.

The last example presenting a completely different approach to use organically grown nanostructures is the usage of DNA as a template for copper-wires. DNA on a Si-Wafer was treated with a copper solution and resulting in conductive copper covered DNA strings. Still there are many irregularities as the thickness of the copper film varies and the location of the DNA is arbitrary. This approach has the potential for further usage as DNA can be targeted with complementary DNA strings and thus the location problem can be overcome. The example demonstrates how the attributes of organic structures can be used creatively in technology.

Organically grown nanostructures are mostly suggested to be used in chip design. This just might be the wrong application for them, as lithography is likely to remain dominant in this field for a long time. The problems listed in the beginning (control of the dimensions, the morphology and the monodispersity) are too important in chip design to be avoided and a solution for them seems to be too far away. One should rather search for other applications which do not require that high accuracy in that area. As there are new devices and phenomena that are only seen on the nanoscale, grown nanostructures could be used to support them. These might be more insensitive to those problems. For the working nanostructures in nature, the proteins, this problem is avoided by two security mechanisms. Firstly, their primary structure is encoded in the DNA. The chemical stability and the mechanisms to protect the DNA from possible changes are a good protection. Secondly, many other proteins are involved in the process of decoding and constructing the new protein, some are just there to control the structure, doing what is called proof-reading. Accidentally wrongly constructed proteins are

disposed. If one could, for example, find a way to order structures like nanorods and -wires by any means, chemically or by any other way, growth would be a little closer to being an alternative production method. Solutions need to be found in integrating grown nanostructures into traditional production methods but also finding ways where their disadvantages are not taken into account that much.