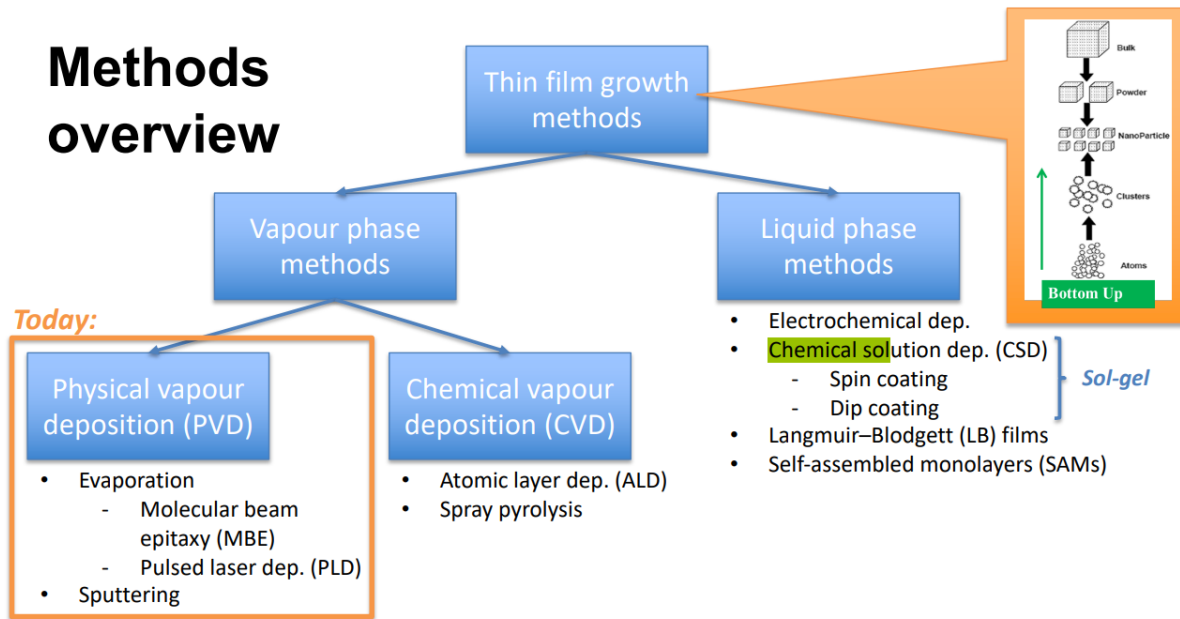


# Fabrication methods

## By dimension

0D nanostructures:	1D nanostructures	2D nanostructures
Nanoparticles Buckyballs Quantum dots	Nano-fibers Nanorods Nanowires CNT's	Thin films Plates Graphene SAMs
<ol style="list-style-type: none"> <li>Sol-gel synthesis</li> <li>Vapour phase synthesis</li> <li>Heterogeneous nucleation</li> </ol> <p><b>Colloidal synthesis</b> <b>Reverse micelle synthesis</b></p>	<p><i>Growth mechanism:</i></p> <ol style="list-style-type: none"> <li><i>Evaporation-condensation growth (VS)</i></li> <li><i>Dissolution-condensation growth (VS)</i></li> <li><i>Vapour-Liquid-Solid (VLS) growth</i></li> <li><i>Solution-Liquid-Solid (SLS) growth</i></li> </ol> <p><b>MBE with VLS</b> <b>Electrospinning</b> Tools like Atomic Force Microscopy (AFM), Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), Near-field Scanning Optical Microscopy (SNOM), Scanning Probe Microscopy (SPM), X-Ray Diffraction (XRD), and Energy Dispersive X-Ray Spectroscopy (EDX) are some of the techniques generally used for this purpose</p>	<ol style="list-style-type: none"> <li>Thin film deposition</li> <li>Physical vapor deposition (PVD) <ul style="list-style-type: none"> <li>MBE</li> <li>PLD</li> <li>Sputtering</li> </ul> </li> <li>Chemical vapor deposition (CVD) <ul style="list-style-type: none"> <li><b>ALD</b></li> <li>Spray pyrolysis</li> </ul> </li> <li>Liquid phase methods: <ul style="list-style-type: none"> <li>Electrochemical deposition</li> <li>CSD: Chemical solution deposition like spin, spray and dip coating</li> <li>Langmuir-Blodgett (LB) films</li> <li>SAMs: Self-Assembled monolayers</li> </ul> </li> </ol>

# Methods overview



## By approach

Bottom-up	In between	Top-down
Colloidal synthesis	Lithography	Ball milling
Sol-gel		Etching
Hydrothermal synthesis		Attrition
Spray pyrolysis		Quenching

## Confined synthesis

Thermodynamically confined	Kinetically confined
Thermodynamically confined nanoparticle synthesis is about controlling nucleation and growth in order to limit the size of the nanoparticles. The nucleation rate should be as high as possible in order to produce small particles (need high supersaturation). The growth rate should be as low as possible in order to limit the growth (dilute solutions).	Kinetically confined nanoparticle synthesis involves the use of "confined spaces" in order to limit the size of nanoparticles. Nucleation and growth considerations are therefore not as important for limiting the size. In a reverse micelle, for instance, there is a small volume containing water where the reaction is occurring, and the size is therefore limited by this space.

## By method

Method	Description	Material
Electrospinning	A viscous liquid (usually a polymer solution) is ejected from an orifice in a strong electric field. When the electric forces overcome the surface tension, a thin jet shoots out from the conical droplet (Taylor cone). The jet is electrically charged, which causes buckling/curling of the fibre. The solvent evaporates, and the fibre is collected on a flat surface or rolled up.	Polymers!!!  Also, polymer/oxide hybrids.  Embedded NPs.
Sol-gel processing  Products: Coatings and thin films, monoliths, composites, porous membranes, powders and fibers	<ol style="list-style-type: none"> <li>1. Sol: Formation of stable solution by hydrolysis and partial condensation of precursor.</li> <li>2. Gel: Formation of metal oxo bonds</li> <li>3. Aging: Condensation continues within the gel, resulting in shrinking and densification along with expulsion of solvent.</li> <li>4. Drying: Water and other volatile impurities are removed from the gel network.</li> <li>5. Dehydration: Removal of surface M-OH groups via calcination at <math>\sim 800</math> °C.</li> <li>6. Thermal treatment: Densification of the gels at temperatures <math>&gt; 800</math> °C via sintering and grain growth</li> </ol>	any oxide composition, but also some non-oxides+ new hybrid organic-inorganic materials which do not exist naturally  carbides, nitrides, and sulfide in inert atmosphere with aprotic solvent
Electrochemical deposition (with templates)	<p>Template method where electrochemical deposition is used to fill the template.</p> <p>A template can be formed either by lithographic methods) or it is possible to for example use commercial alumina membranes with specific diameters. In this process a thin film of a conducting material is first deposited on one side of the membrane. This forms the cathode in the deposition process. The membrane with the conductive film is then immersed in a solution containing a Cu-salt. When a potential is applied, the Cu-ions are reduced and deposited on the cathode. In this case the Cu will only deposit on the conductive surface, meaning it will start to fill up the pores. Since the growth rate is not uniform across the entire surface, the length of the nanorods will vary. But the diameter is determined by the diameter of the pores in the template. The template can later be removed to produce individual free-standing nanorods.</p>	NOT SUITABLE for metals  Specific diameter requirement, not length  Ex: Cu, Ga
Molecular Beam Epitaxy (MBE)	In MBE, catalyst particles (f.ex. gold) are deposited on a substrate. The size of the gold particles can be controlled and thereby controlling the diameter of the nanowires. After deposition of the catalyst particles, the substrate is placed in the reaction chamber of the MBE and ultrahigh vacuum is achieved ( $\sim 10^{-10}$ torr). Knudson cells (resistive	Specific diameter and length requirements

	<p>heating) are used to heat the precursors (Ge) which is in solid form. The evaporated precursor forms the molecular beam which is deposited on the substrate. The gold catalysts particles which are now in a liquid form (heated substrate), are saturated with the precursor. When the particle reaches super-saturation the precursors starts to precipitate on the surface of the catalyst particles.</p> <p><u>Growth mechanism: VLS</u></p> <p>The Ge nanowires proceed to grow by VLS-mechanism and the growth continues as long as the catalyst is kept in the liquid state and precursor is supplied. The growth is very homogeneous across the substrate, and due to the ultrahigh vacuum, the environment is extremely clean, producing high quality nanowires with a narrow size distribution.</p>	<p>MBE – III-IV semiconductors, 2D materials, oxides</p>
<b>Pulsed laser deposition (PLD)</b>	Specific diameter and length requirements.	Specific diameter and length requirements.
Lithography		Create templates
Reverse micelle reactor	<p>Reducing a metal salt chemically</p> <p>Controlling the shape and size by combining the use of reverse micelles and a salt or capping agent</p>	<p>Metals</p> <p>NB: small enough size</p> <p>NB: difficult to get only one shape</p>
PECVD	<p>PECVD is a chemical vapor deposition process used to deposit thin films from a gas state to a solid state on a substrate. PECVD system consists of a vacuum chamber with 2 parallel electrodes. The space between the electrodes is filled with the reacting gases, and a plasma is created between the electrodes. For metallic films, the plasma can be created by Direct Current (DC) discharge between two electrodes. In the case of nonmetallic films, the Plasma is generally created by Radio Frequency (RF). (Alternative Current (AC)). The system operates at pressures in the range 0.13 mbar to 1.59 mbar. In comparison to standard CVD techniques that require 600°C to 800°C, PECVD operates at lower temperatures</p>	CNTs, Diamond thin films
CVD		polycrystalline Si, SiO <sub>2</sub> , SiNH, Tungsten, C-based
PLD	<p>PLD is a physical vapor deposition technique where a high power pulsed laser beam is focused to strike a target of the desired material. Material is then vaporised and deposited as a film on a substrate facing the target. This process can be performed in ultrahigh vacuum or in the</p>	<p>VERSATILE complex oxides YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub>, batteries etc • Sputtering – metals, complex</p>

	presence of background gas, such as oxygen when depositing thin films of oxides.	oxides, 2D materials
ALD	ALD is a cyclic method where monolayers are added one by one	high k oxides: HfO <sub>2</sub> , ZrO <sub>2</sub> , TiN, TaN, Cu interconnects, noble metals, (FRAM, DRAM), TiO <sub>2</sub>
Sputtering		metals, complex oxides, 2D materials
SAMs (Self-Assembled Monolayers)		Organosilicon or alkylsilane on hydroxylated surfaces, such as SiO <sub>2</sub> on Si, Al <sub>2</sub> O <sub>3</sub> on Al, glass, etc. • Alkanethiols on gold, silver and copper • Dialkyl sulfides on gold • Dialkyl disulfides on gold • Alcohols and amines on platinum • Carboxylic acids on aluminium oxide and silver

## By material

Material	Synthesis method
Metallic 1D	<ul style="list-style-type: none"> <li>• Electrochemical deposition onto a substrate with template pattern prepared by lithographic methods with sufficient precision, e.g. EBL.</li> <li>• Electron beam reduction of gaseous Ag precursors.</li> <li>• Dissolution-condensation with a seed crystal and a growth directing agent. VLS is generally not suitable for metallic nanowires.</li> </ul>
Semiconductor 1D	Very suitable for VLS* method using e.g. MBE or CVD for providing suitable Ge precursor molecules. *A metal catalyst with appropriate solubility (from phase diagrams)
Polypropylene 1D	Electrospinning is the obvious choice of method as polypropylene is a polymer, fast and inexpensive method.

Oxide NP's 1D	<p>Spray pyrolysis is an ideal method for preparing large quantities because one can use a continuous reactor and aqueous solvent, thus enabling complex stoichiometries. Nanosized particles are prepared with proper choice of nozzle and furnace temperature. Finally, a naturally arising distribution of particle size is favourable for sintering dense ceramics.</p> <ul style="list-style-type: none"> <li>- scalability/continuous reactor</li> <li>- aqueous solvent enabling complex stoichiometries</li> </ul>
NiAu nanospindle heterogeneous nuc	<p>Seed mediated growth</p> <ul style="list-style-type: none"> <li>- Metallic Precursor, Reducing + Stabilizing agent, Reaction Medium, Seed Molecule, Metallic Precursor</li> </ul>
MCM-41 (mesoporous)	<p>See textbook p.312.</p> <ul style="list-style-type: none"> <li>- sol-gel chemistry with alkoxide precursor</li> <li>- hydrolysis and polymerization/condensation → continuous network.</li> <li>- Template: Surfactants (above CMC) → self-assembly → cylindrical micelles → hexagonal packing.</li> <li>- Heat treatment: remove organics and water.</li> </ul>
Ordered mesoporous materials using surfactants	<p>Surfactant concentration must be controlled and well above the critical micelle concentration. • The surfactant concentration determines if we get micelles, cylinders, layers or multilayered micelles. • Sol-gel synthesis is used with the surfactant structure as a template which determines where the subsequent voids will be, in other words the pore structure. • The final step involves removing the surfactant templates, either by calcining or by solvent extraction.</p>
<p>Core-shell nanowires</p> <p>Ge with diameter = 5-10 nm and the Amorphous silica (SiO<sub>2</sub>) shell 2 nm</p>	<p><u>Core</u>: To produce single crystalline Ge nanorods to be the core of the core-shell wires it is probably a good idea to utilize the VLS (Vapor-Liquid-Solid) method. For the diameter to be about 5-10 nm, the catalyst must have an equivalent diameter. For example, gold NP's (of such a size that gives the wanted diameter when melted) could be used. The first step would then be sputtering these gold particles on a substrate before it is placed in the reaction chamber for growth. Growth of the rods can happen after the gold is heated till they are liquid and can work as a catalyst – and as long as there is enough Ge-precursor present. The supply of Ge can either be supplied by PLD (laser ablation of Ge) or MBE (heated and evaporated Ge which then sublime). The growth time is what determines the length of the produced nanorods.</p> <p><u>Shell</u>: To then cover the already produced nanorods in an amorphous silica shell, they could be dip-coated in a sol-gel-solution of silica, followed by a post-dip thermal treatment.</p> <p><b>Crystalline silica shell</b>: If you have a source of solid crystalline silica, it could be produced directly in a reaction chamber like in VLS using either MBE or PLD to evaporate and then coat the nanorods. Another suggestion could be to heat the nanowire with an amorphous silica-shell until it crystallizes. This could be challenging due to possible reaction/changes in the Ge-core or Ge-silica interface caused by the high temperature needed for crystallization.</p>
Core shell NP's in general	<p>Sol-gel processing</p> <p>Ex:</p> <p>Step1: Synthesis of core</p> <ul style="list-style-type: none"> <li>• Step 2: Deposition of METAL by reduction of XX.</li> <li>• Step 3: Deposition of METAL 2 (precursor) in the presence of SURFACTANT (ex: CTAB) for generating a shell.</li> </ul>

<p><b>Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> core-shell particles</b></p>	<p><u>Core synthesis:</u> The “obvious” method is to precipitate a (oxy)hydroxide, which is then heat-treated/dried to produce the desired oxide. Start by dissolving a 2:1 mix of FeCl<sub>3</sub> and FeCl<sub>2</sub> (Fe<sub>3</sub>O<sub>4</sub> has a 2:1 ratio of Fe<sup>3+</sup> and Fe<sup>2+</sup>) in a water-based phase and add a base (NaOH, NH<sub>3</sub>) whilst stirring. Alternatively, urea can be added, and the solution heated so that OH<sup>-</sup> is released. This gives more control of the reaction (more gentle addition of OH<sup>-</sup>). If a non-polar solvent had been on the list, the reverse micelle method would have been another good option here.</p> <p><u>Shell synthesis:</u> Once the magnetite nanoparticles have been made and exist as an aqueous dispersion, a sol-gel precursor (TEOS) can be added along with a base to catalyse polycondensation, and this will result in a gel forming and encapsulating the magnetite particles. Since the core is an oxide, the particles will have a certain affinity for silica and do not need further functionalisation. This is essentially a heterogeneous nucleation process where silica precipitates on the surface of the magnetite particles.</p> <p>Note that the use of surfactants is not strictly required for either step, but it is often done. In the sol-gel step, micelles can act as nucleation centres, and also contribute to making the silica shells porous in cases where this is desirable.</p>
<p>Nanorods with controlled diameter and length of complex oxides</p> <p>Ex: PbTiO<sub>3</sub> d=200nm, l=50µm</p>	<p>VLS difficult. Hydrothermal synthesis methods? Difficult to control shape and morphology Co-precipitation in reverse micelles would be quite challenging Too big for reverse micelles</p> <p>Sol-gel processing + template method Here, step 1 +2: mixing precursors with solvents and required acid/base and other necessary organics) before the sol is filled in the pores of the template. In this case a commercial alumina membrane can be used. After completing the remaining steps of the sol-gel process, the template can be removed to produce individual nanorods.</p>
<p><b>Zeolites</b></p>	<p>Generally synthesized by hydrothermal process Reagents: – Water – Silica source – Alumina source – Mineralizing agent – Structure directing agent</p>
<p><b>Ordered matrix of quantum dots on a surface in layers</b></p>	<p>The method used to produce the structure shown here was pulsed laser deposition (PLD), but molecular beam epitaxy (MBE) could also be used. PLD is not always as clean as MBE and might therefore give more defects in the structure. However, PLD is often easier to use when more complex compositions such as Ga<sub>0.65</sub>Al<sub>0.35</sub>As are deposited. Here, the source already contains the correct stoichiometry and the material is ablated stoichiometrically from the source and deposited on the substrate. In MBE, several sources must be used to obtain this same material, and it is therefore more challenging to obtain the desired composition, although not impossible.</p> <p>Layers: the continuous layers are formed by depositing a layer (or multiple layers) of the desired material, and the layer grows in the Frank van der Merwe (layer-by-layer) mode. This growth occurs when <math>\gamma_{\text{substrate}} &gt; \gamma_{\text{adsorbate}} + \gamma_{\text{interface}}</math>.</p> <p>The quantum dots are formed by the Stranski-Krastanov mode. In this mode, a continuous layer is first formed, then at a critical thickness the growth</p>



	<p>changes into a three-dimensional island growth. The transition from continuous film to island structure can be quite abrupt in many pairs of metallic or semiconductor systems after the deposition of just a few monolayers. In practice, in the Stranski-Krastanov mode, island formation often results from competition between the surface energy which appears on the island faces and the elastic or plastic energy released in the bulk of the islands and/or the substrate. Stranski-Krastanov mode can be achieved if the lattice mismatch between the substrate and the deposited material is sufficiently large such that the stresses due to this lattice mismatch cannot be accommodated only by dislocations in the lattice.</p> <p>In order to produce the structure shown below, the layer-by-layer growth and the Stranski-Krastanov growth are applied several times in order to obtain the different layers.</p>
<p>Cylindrical crystalline SiO<sub>2</sub> nanorods on glass substrate with d=250 nm, l=500nm</p> <p>Requirements: fast, cheap, simple and reproducible way</p>	<p>Step 1: make a master wafer by f.ex lithography. Make cylindrical rods of a cheap and hard material (ex. Si) with the desired dimensions on a wafer (ex. Si) using lithography.</p> <p>Step 2: make a master mold Deposit a polymer (PMMA, PDMS etc.) on top of the master wafer. After the polymer has hardened, it can be removed and you're left with a mold with cylindrical holes.</p> <p>Step 3: nanoimprint lithography on sol-gel film Press the mold onto a sol-gel film of Si alkoxides on a glass substrate to create a pattern while heating (ca 150 oC) to form a stable xerogel. This mold can simply be lifted off and reused, which is a very important point here!</p> <p>Step 4: anneal Anneal the sample at 500-800 oC to finish the sol-gel reactions and to crystallize the SiO<sub>2</sub>.</p>
<p><b>Spherical gold nanoparticles with tunable size and a very narrow size distribution</b></p>	<p>1. Using a flask, HAuCl<sub>4</sub> (= precursor) is dissolved in water, making a very dilute solution. The solution is heated on a hotplate with a magnetic stirrer to ensure a rapid mixing. A small amount of sodium citrate (=reduction agent) is added while the solution is boiling. This reduces the Au-ions to elemental Au nanoparticles of very small diameter.</p> <p>2. Since the question asked for nanoparticles with a very narrow size distribution, using reverse micelles would give extra points. Using a flask, HAuCl<sub>4</sub> (= precursor) is dissolved in a mixture of water and isoctane (=oily phase) together with AOT (=surfactant) to produce a microemulsion/reverse micelles. The solution is heated on a hotplate with a magnetic stirrer to ensure a rapid mixing. A small amount of sodium citrate (=reduction agent) is added while the solution is boiling. This reduces the Au-ions to elemental Au nanoparticles which is limited in size by the reverse micelles.</p> <p>Note: NaBH<sub>4</sub> can also be used as reduction agent.</p>
<p><b>Co nanoparticles</b></p>	<p>Reverse micelle reactor</p> <p>The two reagents are mixed with hexane, water and surfactant in two separate containers to obtain a dispersion of reverse micelles containing aqueous CoCl<sub>2</sub> and a dispersion of Side 5 av 13 reverse micelles containing aqueous NaBH<sub>4</sub>. The two dispersions are then mixed, and because of Brownian motion some of them will collide and form a short-lived larger reverse micelle. The aqueous cores are thus mixed and a chemical reaction can occur. The reaction that occurs is the reduction of Co<sup>2+</sup> to Co by the reducing agent NaBH<sub>4</sub>. The exact reaction mechanism can be complex and depends on the amount of oxygen present.</p>



	<p>The size of nanoparticles synthesized in reverse micelles can be controlled by the water content because the size of the reverse micelles increases with increasing water content. The size of the resulting nanoparticles will reflect the size of the reverse micelle, at least for smaller reverse micelles (&lt; ~6 nm in diameter)</p>
<p><b>Rh@SiO<sub>2</sub> core@shell nanostructures</b></p>	<p><b>Step1.</b> Synthesis of Rh NPs using the precursor RhCl<sub>3</sub> and the reducing reagent methanol, water is used as solvent.</p> <p><b>Step2.</b> Functionalization of the surface of Rh NPs. As NPs are inert, they do not form a passive layer in solution (such for example OH groups), so they will not react with silica to form the shell. In this case, functionalization of the surface of Rh NPs is required. APS is used to functionalize Rh NPs: Aqueous solution of APS is prepared and added to Rh NPs solution under stirring.</p> <p>pH &gt; 11 → NH<sub>2</sub> with lone pair electrons can bind strongly to Rh surface. In addition to the anchoring of APS molecules on the surface of Rh NPs, hydrolysis and condensation processes take place resulting in the formation of Si-O-Si bridges:</p> <p><b>Step3.</b> Sol-gel process will be used to coat the functionalized NPs with silica (amorphous SiO<sub>2</sub>) the precursor used is TEOS. TEOS aqueous solution is prepared at pH 11</p> <p>Hydrolysis: <math>\text{Si(OR)}_4 + \text{H}_2\text{O} \rightarrow \text{Si(OR)}_3(\text{OH}) + \text{ROH}</math></p> <p>Condensation: <math>(\text{OR})_3\text{Si} - \text{OH} + \text{HO} - \text{Si(OR)}_3 \rightarrow (\text{OR})_3\text{Si} - \text{O} - \text{Si(OR)}_3 + \text{H}_2\text{O}</math></p> <p>Or: <math>(\text{OR})_3\text{Si} - \text{OR} + \text{HO} - \text{Si(OR)}_3 \rightarrow (\text{OR})_3\text{Si} - \text{O} - \text{Si(OR)}_3 + \text{ROH}</math></p> <p>MIX THE SOLUTION → Aging process (24h) with continuous stirring</p> <p>A shell of amorphous SiO<sub>2</sub> is formed around the Rh NPs.</p>
<p><b>Palladium (Pd) nanoparticles</b></p>	<p><b>Reverse micelle as reactor</b></p> <p>Step 1. The PdCl<sub>2</sub> (Palladium (II) chloride) solution is prepared by dissolving PdCl<sub>2</sub> in water, and adding HCl (drop by drop) to obtain a transparent brown solution.</p> <p>Step 2. PdCl<sub>2</sub> aqueous solution is added to Na(AOT) in isooctane. The water-to-surfactant ratio (w) [H<sub>2</sub>O]/[AOT] should be adjusted to a value above 10 to have an access to the r-micelle (solution A)</p> <p>Step 3. A second population of r-micelles containing an aqueous solution of the reducing reagent NaBH<sub>4</sub> is prepared in the same conditions than (step 2) with a ratio w = [H<sub>2</sub>O]/[AOT] above 10. (solution B)</p> <p>Step 4. Solution A and solution B are mixed, then under Brownian motion, the r-micelles will undergo collisions and coalescences and form a short-lived larger reverse micelle. Then the exchange of their content occurs resulting in the formation of Pd nanoparticles</p>
<p><b>Cu nanostructures by the microemulsion method</b></p>	<p>Cu precursor, for instance CuCl<sub>2</sub></p> <p>Surfactant, for instance, cetyltrimethylammonium bromide (CTAB)</p> <p>Reducing agent, for instance hydrazine N<sub>2</sub>H<sub>4</sub></p> <p>Two solvents: toluene C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub> (oily phase) and water H<sub>2</sub>O (aqueous phase)</p> <p>Other methods to produce metal nanoparticles could be precipitation and co-precipitation methods or vapor phase methods, for example by sputtering a Cu target to obtain Cu nanoparticles.</p>
<p><b>ZnS monolayer</b></p>	<p>ALD:</p> <p>Step 1: ZnCl<sub>2</sub> is chemisorbed on the substrate</p>

	Step 2: H <sub>2</sub> S is introduced to the chamber to react with ZnCl <sub>2</sub> to deposit ZnS monolayer on the substrate. HCl is released as by-product and removed from the deposition chamber
<b>Metallic nanoparticles (Pd, Ni, Co)</b>	Electrochemical deposition
<b>Spherical or worm-like Pd nanocrystals</b>	Reverse micelles as nanoreactors
<b>spherical PtFe nanocrystal</b>	Reverse micelles as nanoreactors
<b>Colloidal CdS (Cadmium sulfide)</b>	Growth termination
<b>Ag or Pt nanowires</b>	Dissolution-condensation growth Precursor: AgNO <sub>3</sub> and/or PtCl <sub>2</sub>
<b>TiO<sub>2</sub> nanorods</b>	<b>Electrophoretic deposition:</b> Template based: Electrode: Cu – Template: Polycarbonate membrane prepared by track-etching – Sol: TiO <sub>2</sub> sol – Voltage: 0.3-0.8 V – Time: 60-90 min
<b>ZnO nanofibres</b>	<b>Electrospinning</b> Precursor solution: Polyvinylpyrrolidone (PVP) and zinc acetate dihydrate (Zn(CH <sub>3</sub> COO) <sub>2</sub> ·H <sub>2</sub> O) in dimethylformamide (DMF).
<b>Si nanowires</b>	Lithography
<b>Alkanethiol on Au</b>	SAM
<b>Vanadium oxide nanowires (VO<sub>2</sub>)</b>	Nanoimprint lithography
<b>TiO<sub>2</sub> nanotubes:</b>	The use of templates or hydrothermal synthesis.

## Porous materials

	Example	Synthesis	Applications
<b>Microporous: d&lt;2nm</b>	zeolites	<u>Hydrothermal (or solvothermal) process.</u>  All precursors and reactants are placed in an autoclave. @Elevated temperature and pressure +Mineralizing agent →desired porous network.  Can be combined with sol-gel processing.	Catalysts, Molecular sieves, adsorbents, templates or ion exchange(?).
<b>Mesoporous: d=2-50 nm</b> - Ordered - Random	MCM-series	1. Self-assembled surfactants as template	Supports, adsorbents, sieves, nanoscale chemical reactors

		<p>2. Simultaneous sol-gel condensation around template</p> <p>Ordered: Similar to microporous, but organic structure-directing agent. Micelles or reverse micelles are formed and the framework material is deposited on the outside of the micellar structures.</p>	
<b>Macroporous: <math>d &gt; 50</math> nm</b>	Sponge, soil		

### Thin film growth modes

<b>Frank-van der Merwe (layer-by-layer):</b>	<b>Stranski–Krastanov (island-layer):</b>	<b>Volmer-Weber (island):</b>
In the layer-by-layer mode a new layer only begins when the previous one has been completed, and the successive layers tend to spread out.	Begins with two-dimensional growth and then continues by three-dimensional growth. In this case, the overall interaction energy between the adsorbed atom and the film varies significantly with the thickness of the deposited film, and this transition can be quite abrupt in many pairs of metallic or semiconductor systems after the deposition of just a few monolayers.	In the island growth mode small clusters nucleate directly on the surface of the substrate and the atoms tend to bind to each other rather than to the substrate.
		e.g., a transition metal on a noble metal or an oxide.
$\gamma_{substrate} > \gamma_{adsorbate} + \gamma_{interface}$	Lattice mismatch $\rightarrow$ change	$\gamma_{substrate} < \gamma_{adsorbate} + \gamma_{interface}$

### Sol-gel thin films

<b>Advantages</b>	<b>Disadvantages</b>
<ul style="list-style-type: none"> <li>• Simple and inexpensive</li> <li>• Low processing temperature</li> <li>• For large or complicated surfaces (dip coating)</li> <li>• Easy to scale up</li> <li>• Controlled composition</li> <li>• Homogeneous coatings</li> <li>• Wide range of substrates: glass, plastics, metals, ceramics,...</li> </ul>	<ul style="list-style-type: none"> <li>• Limitation of film thickness due to crack formation</li> <li>• Short lifetime of the sols</li> <li>• Requires an ultimate densification heat treatment</li> </ul>

### Properties at nanoscale

<b>Property</b>	<b>Change</b>	<b>Application</b>
-----------------	---------------	--------------------

Unit cell volume/ lattice parameters	goes down (up for ionic materials)	
Melting temperature	goes down	
Surface area	goes up	
Surface energy	Goes up	
Superparamagnetism	Sufficiently small single-domain ferromagnetic nanoparticles lose their (shape or intrinsic) magnetic anisotropy, which scales with the volume of the particle. With no magnetic anisotropy, the magnetic moment can easily be reoriented by an external magnetic field, so the magnetic response of a superparamagnetic nanoparticle is very large. This is different from conventional paramagnetism (as in magnetic materials above $T_c$ ), where all the individual spins are completely disordered. In the superparamagnetic particle, all the spins are aligned, but they can be aligned in any direction.	Suitable as magnetic resonance contrast agents.  Data storage (small single-domain ferromagnets) - magnetization (up/down) represent bits (0/1). CHALLENGE: limit for how small the physical bits can be (due to superparamagnetism) and therefore a limit to how high information density we can achieve with magnetic data storage.
Phase transition temperature	normally goes down	
Optical band gap	Can go up	
Mechanical properties	with respect to grain size in polycrystals, not actually nanoparticles larger for smaller particles until a lower size limit where it decreases (Hall–Petch limit)	
Equilibrium solubility?	Goes up??	

## Properties characterization

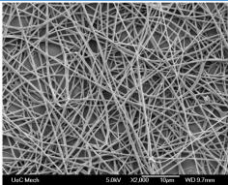
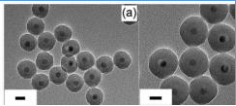
Property	Ideal method	Less ideal methods that can be used
Crystal structure	TEM, XRD	Raman and IR can give some information
Chemical composition profile/element distribution	EELS  <i>STM, SEM, XRD, TEM</i>	SIMS, EDS, XPS and XRF
Surface morphology <i>Morphology</i>	AFM <i>TEM, AFM, STM, SEM</i>	Ellipsometry, SAXS and SEM
Local electric conductivity	cAFM	STM
Ferroelectricity and ferroelectric domain structure	PFM	SEM, TEM, XRD, Raman, SHG
Hardness	AFM	
Topography	AFM, TEM, STM, SEM	

## Need overview of SPM/STM/STEM/TEM flow chart

SEM – samples must be conductive – most electrons absorbed

(S)TEM – transmitted through sample (advantage EELS)

## Characterization techniques

Technique	Material	Information
<b>SEM</b> 		Imaging. Surface topography view, looks 3D.
<b>TEM/STEM</b> 		Both core and shell visible → transmission microscopy. In example: bright field (strong scatter appear dark)
<b>XPS</b>		XPS spectra are obtained by irradiating a material with a beam of x-rays while simultaneously measuring the kinetic energy of electrons that escape from the top 0 to 10 nm of the material being analysed. The photoelectrons generated from atomic core level shells and emitted from the sample are counted and analysed for their kinetic energy. From this the binding energies of these core levels are determined. The atomic core level energies are characteristic for the elements, in addition energy shifts can be used to analyse the chemical bonding state. Quantitative analysis is possible. XPS allows quantification of elements and their chemical state to better than 1%. XPS requires ultrahigh vacuum ( $P < 10^{-9}$ mbar) conditions

## Growth sites

Site	Property
Kink	Strong adsorption
Terrace	Weak adsorption
Ledge	Strong-ish adsorption
Vacancy	Strongest adsorption
Adatom	

	Energy
Corner	Highest = most broken bonds
Edge	Next highest (range on size) bigger = less broken bonds
Facets	Lowest (range on size) bigger = less broken bonds

## SPM: Scanning Probe Microscopy

	STM (Scanning Tunneling Microscopy)	AFM (Atomic Force Microscopy)
<b>Description</b>	Scanning tunneling microscopy (STM) probes a surface using a conductive probe. A high voltage between the surface and the probe cause tunneling of electrons between the tip and the surface. The tunneling current is kept constant by changing the distance between the tip and the surface. Ergo, the measured distance/height will give information about both changes in atomic force of the surface (topography) and changes to the density of states of the surface (i.e different elements)	The surface is imaged by scanning a probe over it. The probe is a very narrow tip attached to a cantilever which can feel the atomic forces, either by measuring the deflection of the cantilever when scanning at constant height, or by recording the height in order to keep a constant force (deflection). Both techniques can be performed with either an oscillating (tapping mode) or static (contact) cantilever. This technique is therefore excellent for obtaining the topography of the sample. The conductivity of the tip depends on what kind of information one wants to obtain.
<b>In common</b>	Scanning probe techniques (information about the topography) Surface sensitive techniques & Narrow tips are used as probes	
<b>Differences</b>	<ol style="list-style-type: none"> <li>Changes the height to keep the tunneling current constant (i.e. feels both topography and differences in conductivity)</li> <li>tip must be conducting</li> </ol>	<ol style="list-style-type: none"> <li>Feels the atomic forces (i.e only topography)</li> <li>tip <b>can</b> be conducting,</li> </ol>

## Electron microscopy

Type of electron	Information	Techniques using type of e <sup>-</sup>
Secondary	3D-like images	SEM
Backscattered	Composition – atomic number Grain orientation	SEM
Auger		
Bremsstrahlung X-ray		
Characteristix x-rays	Chemical composition (EDS maps)	SEM
Elastically scattered	Diffraction and imaging	(S)TEM
Inelastically scattered	Chemical composition (EELS maps)	(S)TEM (scanning transmission microscopt)
Direct/transmitted		

## X-ray scattering

	Information	Material?
XRD / WAXS	Crystallite size, Atomic positions, Lattice parameters	
SAXS	Particle shape, Particle size	

## Gas adsorption

Measured property	Amount (mass or volume) of adsorbed gas as a function of partial pressure.
Calculated property	<ul style="list-style-type: none"> <li>- (Specific) surface area of the sample</li> <li>- Particle size if assuming particle shape (cubic, spherical)</li> </ul>

## Nanotechnology

Concerns	But nanotechnology can solve some problems
<ol style="list-style-type: none"> <li>1. Huge gaps in knowledge concerning risks</li> <li>2. Difficult to detect and remove</li> <li>3. Absence of regulation</li> <li>4. Difficult to predict the effects</li> <li>5. Size-dependent properties</li> <li>6. Higher reactivity</li> <li>7. Changed persistence of particles inside tissues and the environment</li> </ol>	<ol style="list-style-type: none"> <li>1. Water deficiency: decontamination by using porous nanocomposites, disinfection by noble metal (Ag, Au, Cu) nanoparticles for instance embedded in paper filters or desalination with nanomembranes</li> <li>2. Poorly targeted medical treatments: nanoparticles can enter cells and treat them locally instead of having to bombard the whole body with medicine.</li> <li>3. Food waste: better packaging with lower permeability of oxygen and water</li> <li>4. Stinky sports wear: Ag nanoparticles embedded into the fabric have an antimicrobial effect Icing: passive ice removal by superhydrophobic/icephobic surfaces</li> <li>5. Low efficiency of LEDs: the company Crayonano uses GaAs nanorods grown directly on graphene to revamp the UVLED industry.</li> <li>6. Insufficient material strength: nanofillers can improve the strength of almost any material without changing the other properties</li> <li>7. High energy consumption in electronics: by down-sizing electrical components, we need less energy in order to operate them.</li> </ol>

## Particle size determination

Imaging: particle size

Scherrer equation gives crystallite size.

- ➔ If mismatch with image analysis ➔ Polycrystalline particle
- ➔ If match ➔ Single crystalline particle

## Parameter control

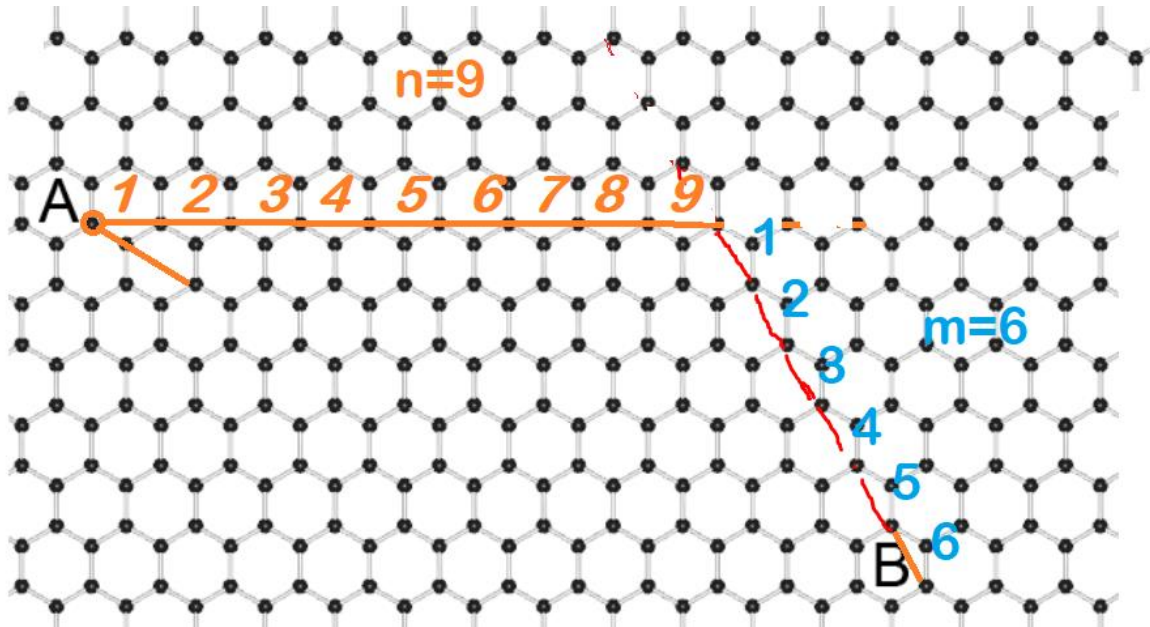
Parameter	How to control it
Size of the core particles	Precipitation: Higher supersaturation leads to more homogeneous nucleation, with smaller size and a narrower size distribution. This is achieved by using higher concentrations of precursors, or by more rapid heating in the case of urea as source of OH <sup>-</sup> . If reverse micelle synthesis is used, the water/surfactant ratio is important (less water gives smaller r-micelles and ultimately smaller particles).
Thickness of shell (silica f.ex)	Thickness increases with increasing amount of TEOS. However, since we are dealing with heterogeneous nucleation, there is a risk if the amount (concentration) of TEOS is too high that primary nuclei will precipitate out, and these will be pure silica particles and not core-shell particles. Finally, enough time must be given for the silica shells to reach an appreciable thickness



**Refluxing time**

Increase → results in a decrease of small particles and an increase of large particles, which is attributed to Ostwald ripening

### How to count for chiral angle in graphene



Metallic if  $2n + m = 3q$ , semiconductor if not

Ex:  $2 \cdot 9 + 6 = 24 = 3 \cdot 8 \rightarrow$  metallic

Deposition	Material	Typical Evaporant	Impurity	Deposition Rate	Temperature Range	Cost
Thermal	Metal or low melt-point materials	Au, Ag, Al, Cr, Sn, Sb, Ge, In, Mg, Ga CdS, PbS, CdSe, NaCl, KCl, AgCl, MgF <sub>2</sub> , CaF <sub>2</sub> , PbCl <sub>2</sub>	High	1 ~ 20 Å/s	~ 1800 °C	Low
E-Beam	Both metal and dielectrics	Everything above, plus: Ni, Pt, Ir, Rh, Ti, V, Zr, W, Ta, Mo Al <sub>2</sub> O <sub>3</sub> , SiO, SiO <sub>2</sub> , SnO <sub>2</sub> , TiO <sub>2</sub> , ZrO <sub>2</sub>	Low	10 ~ 100 Å/s	~ 3000 °C	High