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Precursor directed synthesis – "molecular" mechanisms in the Soft Chemistry approaches and their use for template-free synthesis of metal, metal oxide and metal chalcogenide nanoparticles and nanostructures

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The review provides an insight into the common reaction mechanisms in Soft Chemistry processes involved in nucleation, growth and aggregation of metal and metal oxide and chalcogenide nanoparticles starting from metal-organic precursors such as metal alkoxides, beta-diketonates, carboxylates and their
10 chalcogene analogues and demonstrates how mastering the precursor chemistry permits to control the chemical and phase composition, crystallinity, morphology, porosity and surface characteristics of produced nanomaterials.

To Professor David Avnir on his 65th birthday

15 Introduction

The term Soft Chemistry[1] (or Chimie Douce in French) has emerged in the last quarter of the XXth century as a common notion for the molecular chemistry based approaches to difficult-to-access and usually refractory materials, originally mostly
20 (complex) metal oxides and metal alloys, and more recently also chalcogenides and related semiconductor materials. The name tended to underline the milder conditions utilized in these approaches in contrast to those required by the high-temperature solid state reactions used otherwise in the production of
25 refractory materials. During the last decades and especially with the increased focus on miniaturization of all kinds of electronic equipment and great expectations set on nanotechnology, the Soft Chemistry routes received also broad scale industrial implementation. They have completely replaced, as in the
30 production of coatings and films (see, for example [2]), or inspired a considerable modification with, for example, liquid phase sintering,[3] of the approaches to fine powders and single crystals.

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40 developing molecular precursor chemistry for the synthesis of nanomaterials.*

The development of molecular approaches has early taken strong focus on the use of metal-organic derivatives as precursors due to several reasons. In the gas as well as in the solid phase they display high chemical reactivity and lower thermal stability. In solution, an important advantage lies in application of organic media as solvents. This provides possibility to avoid the challenge of keeping elements with very different acidity/basicity characteristics together in solution and thus potentially broaden the spectrum of accessible chemical compositions.

The studies of chemistry for molecular approaches to the synthesis of, in the first hand, metal oxides were initiated in the early 1950-es by Donald C. Bradley at the Queen Mary College, University of London and were aimed at development of MOCVD synthesis of ZrO_2, HfO_2, Nb_2O_5 and Ta_2O_5 (see [4] and refs therein). The class of compounds he proposed to use for this purpose was metal alkoxides and this effort has set since then major focus on metal-organic precursors such as alkoxide, beta-diketonate and carboxylate derivatives of metals. That is why even this review will pay major attention to application of the salts of organic acids in non-aqueous media, while the reaction mechanisms in the synthesis of metal-based nanomaterials are in many cases very much analogous, for example, for the solution processes in aqueous and in organic media. This may potentially provide an interesting connection to applications in the domain of the entrapment of biomolecules in a matrix of metal nanoparticles and especially chiral metal nanoparticles recently pioneered by David Avnir et al. [5]

The approaches to nanoparticles and nanostructures represent a truly hot topic today and have been a subject of many excellent recent reviews, for example, [6] etc. and thus the focus of the present review is not to provide comprehensive coverage of the materials synthesis but to identify the precursor chemistry based tools in its implementation.

There exists a general consensus that because essentially same precursors are used in the same types of reactions, namely hydrolysis or thermolysis, in all three types of Soft Chemistry processes, occurring in gas (MOCVD and ALD), in solution (Sol-Gel) or in solid phase (MOD), their transformation into nano materials should occur according to analogous mechanisms. The level of maturity and general acceptance of the apparently common mechanistic principles is, however, strikingly different dependent both on the type of the process and the chemical identity of the produced materials. For the solution synthesis of metal chalcogenides, usually applied as and referred to as quantum dots) the ideas about solution equilibrium and heterogeneous kinetics have firmly won the ground and entered the textbooks. For the solution synthesis of metal nanoparticles they became proved and recognized quite recently, due to contributions of S. Sun et al. (please, see the corresponding section below). In gas phase synthesis of metal and metal oxide thin films, especially in the ALD, the analogous mechanisms are proved experimentally but remain a topic of vivid argument. In the Sol-Gel synthesis of metal oxides in spite of unequivocal proof for the same mechanistic scenario, a belief in kinetic control of hydrolysis and polycondensation as the major driving force is still relatively widespread. The aim of the present review is to provide a clear and concise description of the common mechanistic features of different methods used in Soft Chemistry synthesis of metal based nanomaterials.

The mechanisms in Soft Chemistry synthesis of metal, metal oxide and metal chalcogenide nanoparticles

Mechanistic concepts in Soft Chemistry have during long time been generalized starting from the insights in formation of silica (derived from non-metal, metalloid element silicon), where the kinetics of reactions implicated in inorganic polymerization play generally an important role. Understanding of the mechanisms of hydrolysis and condensation reactions in silica-based sol-gel technology opened prospects for many important and spectacular applications in such domains as, for example, stabilization of organic laser dyes,[7] entrapment of enzymes and other proteins for prolonged and improved activity,[8] and creation of "impossible" organic catalysts for complex one-pot acid-base and redox transformations and control of stereospecificity.[9] The mechanisms for formation of metal derived nanomaterials differ, however, considerably from those for silica and, being based on quick and actually reversible reactions, commonly proceed via the state of equilibrium.

Solution reaction mechanisms (Sol-Gel)

Nucleation

Formation of metal, metal oxide and metal chalcogenide nanoparticles in solutions is proceeding via nucleation step leading to most commonly spherical primary particles [10,11] in both hydrolytic and thermolytic processes. Originating either from hydrated metal cations in water solution or from metal-organic precursors in organic media these particles are of course not "naked" but in all the thoroughly studied systems appear to reveal the same general type of construction: a well ordered or even crystalline core demonstrating dense packing of either metal atoms, or cations and anions, and a shell bearing residual ligands acting as interface to the surrounding solution. The latter is responsible for the potential stability of the emerging colloid against aggregation. The formation of a colloid solution is the consequence of the size of the formed species, usually 2-5 nm, exceeding that of the common molecular species. The examples demonstrating the structure of the primary particles become more and more common with the increased interest in these objects and the improvement in Mass-spectrometric and X-ray single crystal determination techniques. They are available now for all the types of nanomaterials considered in this paper.

General approach to noble metal nanoparticles, especially those of Au and Ag is the reduction of water soluble complexes of these metal atoms by sodium borohydride, $NaBH_4$ [12] or sodium citrate (Turkevich synthesis [13]). Another alternative is provided by the thermal decomposition of the metal-organic derivatives or carbonyls of late transition metals in organic media. In both cases the addition of alkylthiols and especially aromatically substituted alkylthiols results in stable-to-aggregation individual nanoparticles covered by thiolate ligands (see Fig. 1).

The composition and structures of the thus produced individual molecular species have been established by a combination of MALDI-TOF mass-spectrometry [14-18] and X-ray single crystals studies.[16]
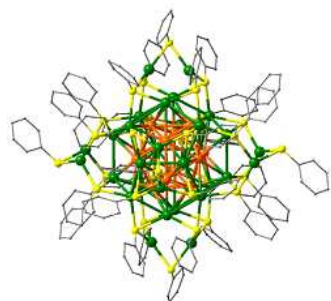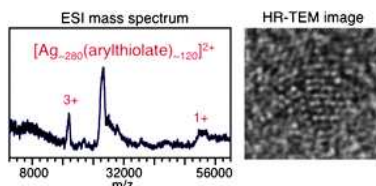
Figure 1. Signals from the Ag_{280} surface-capped nanoparticles in the mass-spectrum along with high resolution TEM image for it (above). Reproduced with permission from ref [19]. Molecular structure of the
5 $Ag_{12}Au_{32}$ nanoparticle capped with phenylthiol ligands from X-ray single crystal study (below). Reproduced with permission from ref[16].

It is very important to note that the thermodynamic equilibrium in formation of metal nanoparticles with this kind of stabilization has been investigated and formation of individual nanoparticle
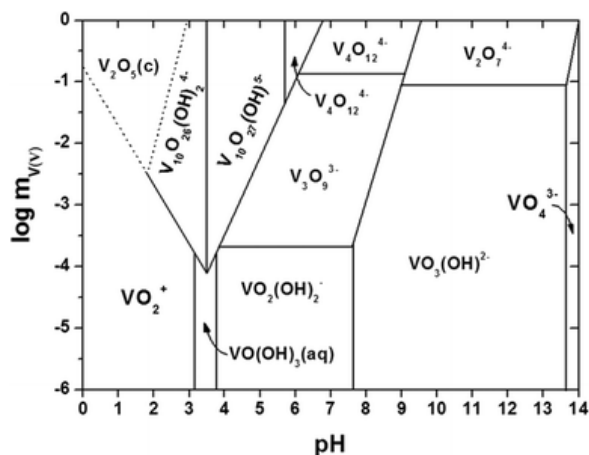10 species in Ostwald ripening process has been established. [19]

Figure 2. Equilibrium diagram for formation of vanadium(V) oxometallate species in water according to ref [22].

Oxide nanoparticles in solution can be produced either by
15 hydrolytic or by non-hydrolytic (thermolytic) route. The processes in aqueous media have been studied in detail first and revealed a situation of complex thermodynamic control, where the equilibrium conditions and the size and structure of the resulting oxometallate aggregates (POMs) were influenced by
20 total concentration of the metal cations, pH and the nature and concentration of the additional complex-forming ligands present in solution (see Fig. 2 for the formation of biologically important polyoxovanadate species in solution, see, for example, [20-22]). The structures of the cores in the forming POMs are revealing the
25 same principle as in metal particles – in this case a dense packing of metal cations and oxide anions, resulting in occurrence of the same structures for the species of widely different chemical origin, for example, Keggin structures for both molybdenum and

tungsten oxometallate anions and the aluminium-based
30 oxometallate cation. [23]

The forming species are relatively small in size at low metal concentration, but for higher concentrations and especially for less acidic metal cations they achieve several nanometers in size and behave as colloid particles. An interesting example has
35 recently been discovered for Ti(IV), where the dilution of solutions of the tetranuclear oxo-carboxylato- titanate complexes especially by less polar solvents such as alcohols results in spherically shaped polyoxometallate cores covered by chelating carboxylate anions. The size of the identified oxo-lactato-titanate
40 anions is rather exactly 3 nm in diameter permitting to reveal the structure of the core as anatase by X-ray diffraction (see Fig. 3).[11] Even in this case the formation of oxide nucleus as individual molecular species resulting from coordination equilibrium has been demonstrated.
45 The role of oxometallate ions as nuclei of oxide phases in the hydrolytic and especially hydrothermal processes leading to formation of oxide minerals in nature has been revealed and investigated in detail in the recent works of William Casey et al. [24,25]
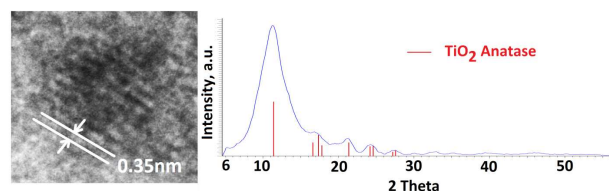

50
Figure 3. High resolutiom TEM image of a Lactato-oxo-titanate species/particle with anatase core structure (left), and the X-ray diffraction pattern of the gel obtained by separation of such particles (right). [11]

55 The hydrolytic processes in organic media are for the metal oxide precursors quick and reversible (until the phase separation takes place), leading even in this case to oxometallate species resulting from coordination equilibrium. Quite long series of partial hydrolysis have been investigated for both homometallic such as
60 $Ti(OR)_4$,[26-28] $Zr(OR)_4$,[29-31] $Nb(OR)_5$ [32,33] and heterometallic alkoxide precursors in the Ni-Sb,[34] Mn-Sb,[35] Ba-Ti,[36] Ba-Zr,[37,38] Ba-Nb[38] and Ba-Ta[38] systems, revealing consequently the same principle: formation of a well-defined densely packed metal oxide core, often mimicking the structure of the corresponding metal
65 oxide, surrounded by a less defined layer bearing residual organic ligands. A very important observation that resulted from success in the structural characterization of all the members of these numerous series was that the structural transformation in general did not keep any memory of the previous step, but followed the
70 core types known otherwise from the structures of oxometallates formed in the aqueous media. Same densely packed motifs appeared in the structures of chemically very different species. Transformation on each step of increase in the hydrolysis ratio (just one of the parameters affecting the equilibrium) can be
75 rather drastic. A very illustrative example is provided by the microhydrolysis of bimetallic M(II)-Ti(IV) beta-diketonato-alkoxides such as $Ni_2Ti_2(acac)_4(OEt)_8$:

$$5Ni_2Ti_2(acac)_4(OEt)_8 + 2H_2O \longrightarrow 2Ni_5TiO(acac)_6(OEt)_6 +$$
80 $$+ 8Ti(acac)(OEt)_3$$
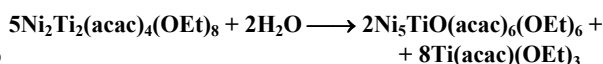
Addition of small stoichiometric or substoichiometric amounts of water reslults in the structure change for the densely packed core in the molecule from tetramolybdate to Lindqvist type of polyoxometallate construction and also changes the ratio between constituent metal atoms from Ni:Ti = 1:1 to 5:1! The reaction has a quantitative yield and is observed for M(II) = Ni, Co, Mg (see Fig. 4). [39,40]

The role of ligands in the formation of the primary particles was found to be in facilitation of the hydrolysis-polycondensation and also stabilization of the emerging particles in solution against aggregation through enhanced interaction with the solvent molecules surrounding them (the direct kinetic data show that the speeds of hydrolysis and polycondensation objectively increase when chelating heteroligands are introduced in the precursors).[29,41] It can be said in simplified manner that the ligands act as surfactants in stabilization of the particles and quantitative evaluation of this role has been reported.[42] The particles are thus both individual molecular entities and also colloid particles stabilized in solution by interaction between the ligands and the solvent by the forces typical for colloid systems, which led to proposal to denote them as Micelles Templated by Self-Assembly of Ligands (MTSALs).[39]
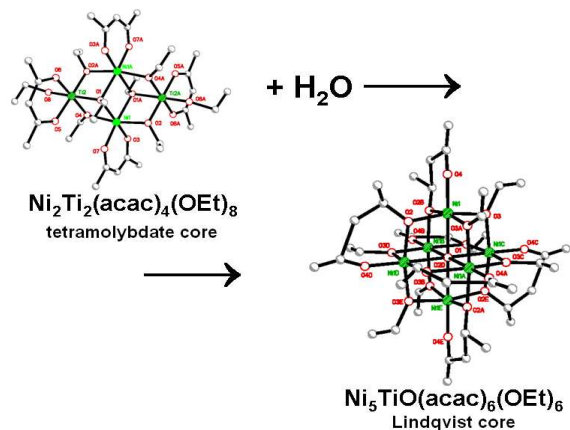

Figure 4. Hydrolysis-condensation transformation of Ni-Ti beta-diketonato alkoxide: transition from a tetranuclear to hexanucler oxometallate core. Reproduced with permission from [43].

The non-hydrolytic (including solvothermal) processes [38,44-47] are in their nature quite analogous to the hydrolytic ones, but at higher temperature they are offering particles that are much more completely crystalline and also the surface ligand-containing layer which is much thinner and less chemically reactive. It has been observed experimentally that the particles of the same material produced from the same precursor, for example, Fe_3O_4 obtained by solution thermolysis of $Fe(acac)_3$, are hydrophobic when obtained from non-polar solvent like xylene,[48] but hydrophilic and easily dispersible in water when synthesized in a polar one like acetophenone.[49] The reason for this difference is the different nature of residual ligands on the surface of the particles. The hydrophilicity and hydrophobicity of the particles can readily be modified by intentional grafting of ligands on the surface of the already produced particles.[50,51]

The uniform nucleation is in fact a well-recognized mechanism for the formation of metal chalcogenides – most commonly sulfides, selenides and tellurides of divalent elements, M(II) = Zn, Cd, Sn, Pb and also nitrides, phosphides and arsenides of trivalent elements, M(III) = In, Ga.[52-54] They are more known today under the name of quantum dots because of the attractive physical and specifically optical properties of the nanoparticles of relatively narrow band semiconductors. Their most important feature is the strong luminescent properties with the color of emitted light strongly dependent on the size of the particles. The size of quantum dots can relatively easily be controlled through the time of solvothermal treatment (please, see below).
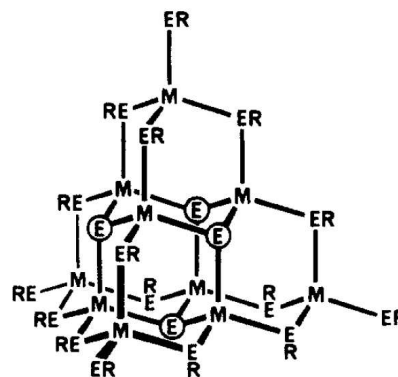

Figure 5. Schematic representation of the molecular structure of $[M_{10}E_4(E'Ph)_{16}]^{4-}$ ions, M = Zn, Cd; E, E' = S, Se, Te, molecular models of the as-obtained quantum dot ME nanoparticles. [10,55] reprinted with permission from ref [55].

The particles originate as MTSALs (with wurtzite type core structure) and require ligands for their stabilization.[55,56] To form uniform and solution stable bigger particles the ligands possessing surfactant characteristics such as Tri-octyl-phosphine oxide have to be added. An alternative is to use metal-organic precursors already bearing useful ligands and even (see below for more detail) single-source precursors.[10,56]

Particle growth – the effects of Ostwald ripening

The step normally following the phase separation of solid material from solution is the Ostwald ripening, called historically also once upon a time an "isothermal distillation". Its effect consists in partial re-dissolution of the "precipitated" material, which affects mostly the particles with relatively higher surface energy, i.e. the smallest ones, with subsequent re-precipitation onto the already existing nuclei, i.e. bigger particles with lower surface energy. The prerequisite is thus of course that there is at least some noticeable dissolution of the precipitated materials like the one for metal oxide particles in acidic aqueous medium or in organic media for noble metal particles in the presence of phosphines, or alternatively for oxides in the presence of acidic ligands, acids or beta-diketones released on solvothermal decomposition. The consequence of this process is that the size of the particles increases and their surface area decreases. The latter effect originates not only in the increase in the radius of the (originally spherical) particle. It can and most often does relate to the change in the shape of the particles. The spherical shape coming from minimization of the surface energy through maximal interaction with the solvent can convert into a polyhedral one with lower surface area. This happens if the crystallographic energy of interaction within the crystal is considerably higher than that between the ligands on the surface

and the solvent. In this case the spherical shape, which can be considered in principle as a crystal with only higher face indices exposed, will transform into the one with lower and lower face indices.

This transformation has been followed by many authors [57-59] for Fe$_3$O$_4$ nanoparticles formed originally as spherical from practically any synthetic approach. On prolonged solvothermal treatment in the absence of strongly coordinating ligands the spherical primary particles grow and turn first rhomboidal or octahedral with 110 faces exposed and then cubooctahedral and finally cubic with 100 faces on the surface. The same effect as the time in thermal treatment can be observed in the same system at room temperature for the polarity/basicity of the reaction medium – from spherical shape at lower pH (6) to octahedral at pH over 8 and finally cubic at pH over 9.[10]

Aggregation – oriented attachment vs coalescence

Formation of bigger particles and structures in the solution synthesis can be a result of aggregation. In fact that is aggregation – sticking of the primary particles together that stays for the sol-gel transition in metal oxide systems. The TEM studies carried out on the aggregates produced under different conditions reveal common features in these processes for both metal, metal oxide and metal chalcogenide particles. If the particles are mostly crystalline in their structure, the aggregation occurs commonly as oriented attachment, i.e. the particles connect to each other in the way keeping the orientation of the atomic layers in the structures (seen as fringes in the TEM images) largely unchanged.
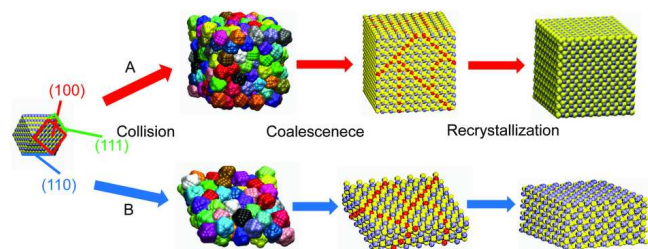

Figure 6. The oriented attachment mechanism (in formation of FeS$_2$ nanocrystals with unexpected symmetry, Reproduced with permission from [62]).

As the result a single crystal like structure is emerging. Because the primary particles are in nanometer range in size, the product of this process is a mesoporous single crystal material. Such materials have been in fact observed and reported for all the classes of compounds covered by this review: metals and alloys, metal oxides, in particular, cerium dioxide – formed with high crystallinity already from the hydrolytic synthesis in aqueous medium[60] and also ZrO$_2$ in the long-term high-temperature solvothermal synthesis,[61] and even for quantum dots.[10, 56] The material can then recrystallize on, for example, thermal treatment, and offering bigger size single crystals (see Fig. 6).

When the emerging primary particles are covered with a relatively thick layer of amorphous material as it happens, for example, in the metal oxide sol-gel synthesis, the aggregation occurs as coalescence/fusion of the primary particles. The inner part of the aggregates remains in these cases mesoporous,[63-65] but the surface densifies to become a continuous film. This is the morphology of a metal oxide gel usually produced by sol-gel

technology. When droplets of metal-organic precursor solution in an organic solvent are injected into water this structure becomes even more complex: the outer surface is covered by a continuous layer while inside the phase separation of the organic solvent creates macropores in the otherwise mesoporous construction formed by coalescence of primary particles.[64,65] The then dried and mildly thermally treated product shows very small open porosity, but it increases greatly after mechanical crushing/milling.[66]
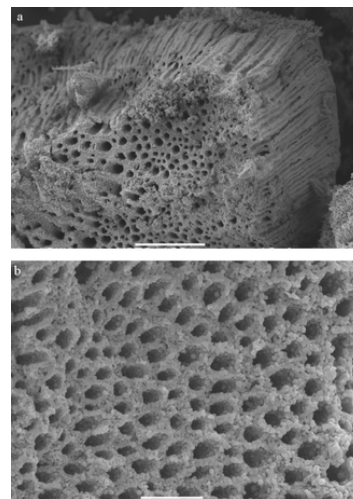

Figure 7. Hierarchically porous inner structure of TiO$_2$ gels produced from Ti(O^{i}Pr)$_4$ (a, scale bar 100 µm) and Ti(O^{n}Bu)$_4$ (b, scale bar 5 µm) by dropping them into aqueous ammonia. Reproduced with permission from ref [65].

Solid state reactions (MOD)

The reactions dealing with decomposition of metal-organic precursors start commonly with solid material and can on heating occur either as a solid state reaction or proceed through melting stage or, alternatively, involve at least partial evaporation with gas phase transport as essential part of the transition mechanism. The way the decomposition occurs is very much dependent on the conditions of thermal treatment.

Quick heating up favors kinetically the phase transitions in the molecular precursors, i.e. melting and/or evaporation, as they are associated with lowest activation energies. Slow heating favors the thermodynamically preferable transitions associated with decomposition of organic ligands and formation of the target material. The processes in melt are quite analogous to those in solution (please, see above), while those involving evaporation are related to the gas phase mechanisms discussed below.

The outcome of the solid state reaction is dependent on the facility of nucleation and growth of the target phase. In the cases when nucleation is facile the formation of highly crystalline nuclei, small nanoparticles in the size range 3-10 nm, can be expected on slow heating of the precursor (typically the heating rate 5°C/min or lower) as it happens, for example, for the formation of Mo$_{1-x}$Re$_x$O$_2$,[67] while when nucleation is hindered the material can remain amorphous to quite high temperatures to be then transformed into a monolith consisting of larger crystals as it happens in Nb and Ta based oxides.[68]
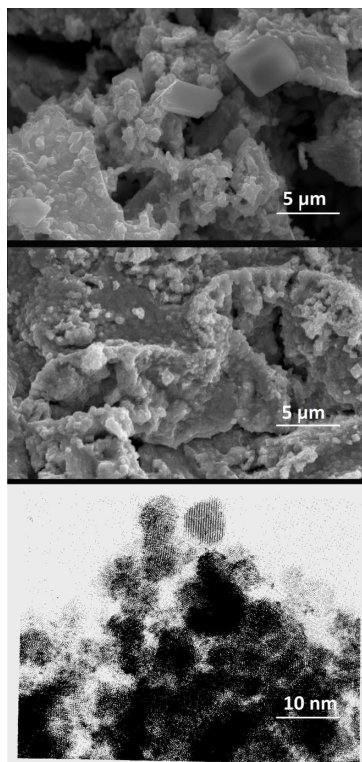
Figure 8. Different processes for ReO$_3$ synthesis by MOD of a rhenium alkoxide Re$_4$O$_6$(OMe)$_{12}$ dependent on the heating rate: gas phase transfer contribution for 20°C/min (upper image), liquid phase (melt) transfer at 10°C/min, and solid state only reaction resulting in small nanoparticles (below). Reproduced with permission from ref [67].

Gas phase processes (MOCVD, ALD and RAPET)

The processes of deposition from the gas phase originally have been considered as belonging to three rather different types dependent on the reaction conditions. The Metal-Organic Chemical Vapor Deposition was typically described as a thermolytic decomposition process in which (a potential excess of) precursor was passed over a substrate heated to a temperature higher than its estimated thermal stability limit. The target coating phase is then nucleating on the surface and the nuclei grow subsequently into relatively uniform crystals randomly covering the substrate surface. The surface of such coating becomes more-and-more rough when the deposition is going on. The film can well be epitaxial (or close to) if its orientation is dictated by the crystal structure and orientation of the substrate. Polycrystalline substrate results normally in production of polycrystalline films. Atomic layer deposition, denoted originally as "molecular beam epitaxy" by Kozyrkin et al.,[69] (for contemporary overview see [70]) was thought from the beginning to be a molecular type process, where an active surface is chemically reacting with a precursor in a monolayer and makes a single layer of the product compound for each precursor pulse. The film in this case was expected to be a true single crystal material (truly epitaxial). The recent high resolution microscopy studies (especially Field Emission SEM and AFM ones) of the films produced by ALD show, however, that the nature of the process is principally different. A true single crystal should have nucleated as a single substrate-wide nucleus, while the reality is that the applied kinetically facile chemical reactions such as

thermohydrolysis [71] or ester elimination [72] lead to facile nucleation of the phase of coating material on the substrate. The latter is then fully covered by the emerging nuclei, which grow uniformly in the diffusion-limited conditions of low-concentration pulses of precursor or activating reagent, e.g. water vapor for thermohydrolysis, as it has been demonstrated in the pioneering works of Steven M. George.[73-75] The resulting film is rather uniform in this case (see Fig. 9).[76,77] Annealing of the film can result finally in a practically single crystal state for the film. Both MOCVD and especially ALD are traditionally processes carried out at lower pressure. In the cases when nucleation of the target phase is facile and the nuclei grow in an oriented fashion, the low pressure is not a pre-requisite. Thus ambient pressure MOCVD has recently been reported for the deposition of relatively thick ZnO [78] and copper metal [79] films.
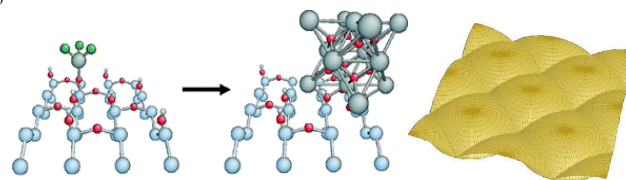

Figure 9. Nucleation of HfO$_2$ on SiO$_2$ surface by pulsed ALD with HfCl$_4$ and H$_2$O (left), reproduced with permission from ref [76]. ALD coating of ZnO on Al$_2$O$_3$ single crystal substrate resulting from coalescence of islands, Reproduced with permission from [77].

The Reaction under Autogeneous Pressure at Elevated Temperatures (RAPET)[80-83] is a gas phase process organized in a way quite different from both MOCVD and ALD but has in its mechanisms a hidden but distinct relationship to both. RAPET is carried out by quick evaporation of large amounts of metal-organic precursor in a small high-pressure sustaining vessel. The applied high temperature sets on a cascade of decomposition reactions often involving reduction of the metal atoms with simultaneous release of water vapor and thus in parallel also thermohydrolysis. The nucleation becomes facile under these conditions and either metal or metal oxide nuclei are instantaneously formed. The precursor disappears thus from the gas phase and the formed nanoparticles initiate carbonization of organics on their surface (see Fig. 10).
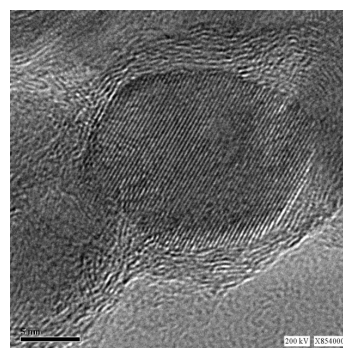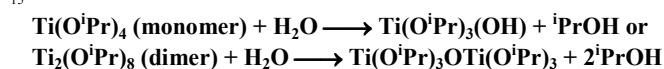

Figure 10. Single nanocrystal of tetragonal ZrO$_2$ in a graphitic shell produced by RAPET of a Zr alkoxide precursor. Reproduced with permission from [82].
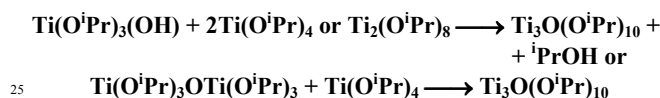
Mechanisms – molecular or not?

The title of the present review is promising molecular mechanisms, but, as one can see, the crucial processes in Soft
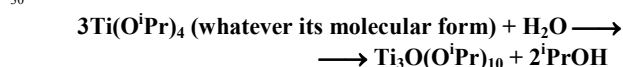
Chemistry are not of molecular nature. They are dealing with already formed metal, oxide or chalcogenide particles even if these particles are covered by ligands and can be considered as huge molecules most often still involved in coordination
5 equilibrium until they aggregate and undergo phase separation. How do they emerge? The precursor molecules are quite small – how do they transform into these big aggregates? Of course, they are undergoing thermolytic or hydrolytic transformations, but because the outcome of these reactions is under thermodynamic
10 control, the exact sequence of them does not play any role. If we add water in substoichiometric amounts as water vapor or diluted solution into a solution of $Ti(O^iPr)_4$ (existing there in a monomer-dimer equilibrium) it will supposedly originally generate within less than a microsecond either an OH-group or an oxo-bridge:

15

$$Ti(O^iPr)_4 \text{ (monomer)} + H_2O \longrightarrow Ti(O^iPr)_3(OH) + {}^iPrOH \text{ or}$$
$$Ti_2(O^iPr)_8 \text{ (dimer)} + H_2O \longrightarrow Ti(O^iPr)_3OTi(O^iPr)_3 + 2{}^iPrOH$$

The produced intermediates will then within less than a
20 microsecond react with excess of the alkoxide to provide the thermodynamic product, trimeric titanium oxo-isopropoxide:

$$Ti(O^iPr)_3(OH) + 2Ti(O^iPr)_4 \text{ or } Ti_2(O^iPr)_8 \longrightarrow Ti_3O(O^iPr)_{10} +$$
$$+ {}^iPrOH \text{ or}$$
25
$$Ti(O^iPr)_3OTi(O^iPr)_3 + Ti(O^iPr)_4 \longrightarrow Ti_3O(O^iPr)_{10}$$

Whatever the sequence of these processes, it will result within the scale of any today available research technique in one and the same total reaction:
30

$$3Ti(O^iPr)_4 \text{ (whatever its molecular form)} + H_2O \longrightarrow$$
$$\longrightarrow Ti_3O(O^iPr)_{10} + 2{}^iPrOH$$

The formed trinuclear molecule follows the structure type of
35 trimolybdate, one of the simplest oxometallate cores. If an excess of water arises locally due to any reason (but no precipitation of the TiO_2 aggregates occurs yet), the produced poly-oxo-metallate will react then with the excess of the alkoxide, $Ti(O^iPr)_4$, resulting in the same final product, $Ti_3O(O^iPr)_{10}$. The processes
40 of ligand transfer in precursor species that cause this return to equilibrium are well studied since long time ago and were first reported in detail for aluminium derivatives by Geoffrey Wengrovius et al.[84] The classic mechanistic studies of John Errington et al. demonstrated that alkoxide ligands can be
45 transferred back to "oxide" species in organic media quickly on NMR scale [85]:

$$WO_4{}^{2-} + WO(OMe)_4 \longrightarrow W_2O_5(OMe)_4{}^{2-}$$
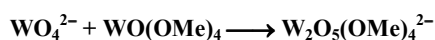
50 The intermolecular transfer of chelating ligands for the derivatives of Zr and Hf has been reported in detail in the works of Gerald Spijksma et al..[29,31,41] Recently we have reported this phenomenon in equilibrium formation of spherical lactato-oxo-tianate species 3nm in size.[11]
55 Even the hydrolytic ALD processes are of course not simple molecular ones: as soon as we get, for example, the first M(IV) center onto a surface of hydroxylated silicon substrate, the proton(s) from the nearby Si-OH groups, which are relatively acidic, will be rapidly transferred onto the more negatively
60 charged ligands at the M(IV)-atom and the further process will continue there, creating a M(IV) oxo-"cluster" instead of monolayer coating in the ALD synthesis of $M(IV)O_2$ high-k dielectrics. Molecular model studies for M(IV) catalytic centers on silica surface, earlier considered as mononuclear ones, turned
65 even them to be "clusters", i.e. oligonuclear species in reality.[86]

Exploitable precursor-directed effects in the synthesis of nanomaterials

Major effort in the large scale synthesis of nanomaterials is today very much focused on application of sometimes quite expensive
70 templates. Removal of the latter represents also a costly and time-consuming step in preparation of materials with controlled porosity, morphology and crystallinity. Applying the insights into reactivity of molecular precursors and the role of ligands they contain or are modified with, permits to propose relatively simple
75 and cost-efficient approaches to highly attractive materials with applications in adsorption and filtration, Li-ion batteries and solar cells, and also in biology and medicine.

Control of crystallinity

The whole Soft Chemistry domain that originated as such from
80 the works on the synthesis of metal oxides by Tishchenko (Al_2O_3 [87]) and Smakula (TiO_2 [88]) was very much influenced in the 1980-es by the then flourishing chemistry and applications of silica derived materials. This was leading to perception that the reactions employed for synthesis of metal oxides by hydrolytic
85 and even non-hydrolytic approaches should offer amorphous materials, requiring post-synthesis annealing to achieve crystallinity. In reality the mechanisms leading to formation of nuclei of metal compounds-derived target phases in all Soft Chemistry techniques are very different from those for formation
90 of covalently bound silicon compounds. The emerging nuclei of metal, metal oxide and metal chalcogenide phases should simply have well defined ordered structures closely related to those of the corresponding bulk materials. This may sometimes be challenging to establish by X-ray diffraction because it is
95 requiring certain size of symmetry-correlated domains (smaller for heavy metals, much larger, up to 5 nm for oxides) and is quenched by structure defects if small domains. Electron diffraction is much more sensitive and reveals order in the systems sometimes looking amorphous under X-ray.[89]
100 The ways to improve crystallinity are thus quite obvious – it is necessary, on one hand, to increase the size of the nuclei and remove components of the amorphous shell, surrounding the crystalline core, and, on the other hand, eliminate the defects in the core by facilitating diffusion of the metal cations.
105 Pursuing the first of these principles it is possible to say that the weaker the ligand is bound to the core, and the less is the energy of its interaction with the solvent, the smaller is the amorphous ligand-containing shell and the bigger in relation is the crystalline core. This observation is quite general and has been demonstrated
110 in solvothermal synthesis for metal particles in the works of Shouheng Sun [90] and for metal oxides by our group.[91] The use of phosphine ligands strongly interacting with palladium atoms leads to smaller ordered domains and practically amorphous particles, while that of less strongly binding amine

ligands offers practically fully crystalline particles. It is important to note that particles are products of coordination equilibrium (MTSALs) and the process turns reversible – can be shifted by excess of an added ligand in the desired direction.[90]

In the same sense using a precursor system with smaller and less thermally stable ligands in the solvothermal synthesis of oxides is preferential when the better crystallinity is the aim. The size of the particles and crystallinity appear not to be dependent on the application of surfactants. For example, fully crystalline maghemite gamma-Fe_2O_3 nanoparticles about 4 nm in size were obtained from the solvothermal reaction of an alkoxide precursor, $Fe(OC_2H_4OCH_3)_3$ in xylene independently whether some amounts of oleic acid were added or not.[48] The role of ligands was demonstrated most apparently in the solvothermal synthesis of $BaTiO_3$ in acetophenone.[91]
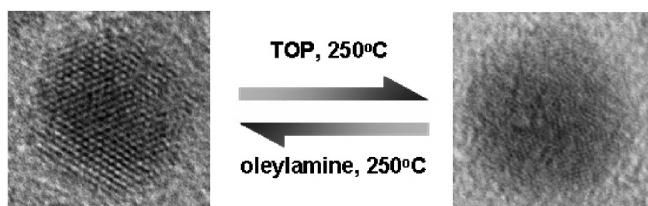

Figure 11. Amorphization-crystallization equilibrium for Pd particles shifted by surface-binding ligands by Sun et al. Reproduced with permission from [90].

Thus refluxing a mixture with ethoxide precursors $Ba(OEt)_2$ and $Ti(OEt)_4$ in 1:1 ratio produced crystalline $BaTiO_3$ at 200°C in acetophenone, while same treatment of a bimetallic single-source beta-diketonate-alkoxide precursor $Ba_2Ti_2(thd)_4(OEt)_8(EtOH)_2$ gave under same conditions a carbon-rich product amorphous by X-rays. The use of aprotic solvent is preferred compared to a protic one, if crystallinity is the aim, of the same reason. The synthesis of $BaTiO_3$ from alkoxides in benzyl alcohol [92] under same conditions as in [91] gives a mostly amorphous product by XRD still requiring after-annealing for crystallization. The temperature plays also a crucial role, of course, as it facilitates diffusion of metal cations. The most facile reaction of ligand removal is achieved for alkoxide precursors of $BaTiO_3$ in allyl alcohol in agreement with the Bradley reaction mechanism,[44,45] but the product is still not fully crystalline when obtained from the synthesis at 100°C.[91]

Removal of organic ligands and curing of the defects can be achieved even by increasing the polarity of the medium and facilitating protolytic mechanisms by applying extreme pH. Thus fully crystalline particles of $BaTiO_3$ (see below for morphology and particle size control) can easily be produced at 90°C by introducing titanium alkoxides into aqueous solution of the strong base $Ba(OH)_2$.[93] The same effect is achieved in the reported techniques for improvement of crystallinity in TiO_2 by peptization: "re-dissolving" in HNO_3 the XRD amorphous precipitate from hydrolysis of titanium alkoxides provides a stable sol consisting of uniform anatase nanoparticles.[94]

In many cases the polarity of water as solvent is enough if the ligands are volatile and removed under reaction conditions. Immersion of solid titanium alkoxide precursors was pioneered by the group of Stephane Daniele for production of single anatase nanoparticles.[95,96] The applied precursors were modified with hydrophilic amino acids to facilitate separation and stabilization of the produced particles, but the latter remained partly amorphous because of the presence of residual ligands. Using titanium methoxide, $Ti(OMe)_4$, as precursor it turned possible to provide fully crystalline anatase with quantitative ceramic yield just by 30 min reflux in water as MeOH was completely removed from the formed nuclei.[97]

Control of nanoparticle morphology/shape and optical properties

The aim of controlling the geometrical shape of nanoparticles emerged in the first hand in the synthesis of metal and metal chalcogenide materials in the view of their important optical properties, plasmon resonance and luminescence respectively. These characteristics are especially important in connection with potential use of these particles in bio-imaging and, for metal particles, even as triggers in optothermal opening of drug delivery vesicles.[98-100] The crystal structure symmetry for the bulk phases of the target materials is mostly truly high, cubic or hexagonal, while the most exciting optical effects are obtained from highly anisotropic materials – rods, dogbones, tetrapods, etc. (see [6]). As we could see above, the simple Ostwald ripening would be of no help to produce such shapes from original spherical nuclei. Solution to the problem lies in finding ligands possessing enhanced affinity to some specific faces of the emerging crystal structure and capable to hinder growth of the crystal in these specific directions.

Preparation of gold nanoparticles with different shapes was achieved most often by a seeding technique where initial spherical particles were introduced then into precursor solution (usually $AuCl_4^-$ for gold) with reducing agent and a surfactant or surface active polymer. Turkevich synthesis with citrate as reducing agent was usually a standard.[101] The growth of anisotropic structures was attributed to the affinity of the nuclei to surfactant or polymer micelles.[102-104] Anisotropic structures were prepared successfully even in the absence of seeds, when a mixture of less and more polar solvents (along with a micelle-forming polymer) was used as medium.[105] The breakthrough was achieved by Schatz et al. who pioneered the use of mixtures of reducing agents, for example, citrate and hydrogen peroxide at room temperature, and application of strongly and weakly bonding ligands in combination, such as citrate and bis(p-sulfonatophenyl) phenylphosphine dihydrate dipotassium (BSPP) for generation of complex anisotropic structures, in particular tetrapods.[106,107] The use of reducing ligands binding specifically to distinct faces in the growing crystal permitted synthesis of anisotropic metal structures in complete absence of surfactants.[108,109] Same kind of approaches – the use of surfactants[110] alternatively the use of specific ligands [10] have been utilized for the synthesis of anisotropic chalcogenide particles. Particles with composition different from the original and with preserved anisotropic shape were accessed by cation exchange reactions.

An important challenge in controlling the shape of nanoparticles is actually preventing them from agglomeration, aggregation and finally coalescence. These phenomena are of less importance in solvothermal synthesis, where the emerging particles have very thin amorphous shell and are mostly crystalline making coalescence possible only on rather long thermal treatment and at

relatively high temperatures.[61] In hydrolytic synthesis of oxides the sticking of particles together does not require high activation energies and is a real hinder to production of uniform particles. Two strategies exploiting the MTSAL mechanism have been 5 developed – hydrolysis of alkoxide precursors by quick mixing with water [112] and alternatively – slow hydrolysis by water vapor.[113-115] The principle behind both approaches is conversion of the whole precursor into nuclei insoluble in the applied solvent. Both very slow and very quick addition of water lead to 10 its uniform distribution and thus uniform equilibrium conditions for the production of polyoxometallate cores. The size of the nuclei is quite logically noticeably bigger for the slow addition of water as it leads to growth of the oxometallate species in the stepwise equilibria. An advantage for the latter approach is 15 provided by the ligands strongly interacting with the solvent – longer chain alcohols or functional alcohols (alkoxy- and amino-ones). The latter are especially attractive due to their superior ability to solvation of metal oxides' particles. Another means in stabilization of particles especially in less polar solvents is 20 application of ligands with bigger alkyl group, such as, for example t-butoxides[116,117] and neo-amyloxides.[118]

A separate challenge is the preparation of uniform microparticles of perovskite oxides, in the first hand $BaTiO_3$ for application in capacitors. It has been answered in the middle of 1980-es in the 25 works of M. Klee et al. at Philipps,[93] who proposed to first produce microparticles of TiO_2 and then introduce them into hot solutions of $M(OH)_2$, M = Sr, Ba. This approach has even been recently re-invented.[93] The role of strongly coordinated inorganic ligands in stabilization of oxide nanoparticles and creation of 30 microparticles has been discussed recently in [119].

Strong affinity of chelating ligands to surface complexation, offering protection of the particles against aggregation, gave recently rise to an astonishing idea to create particles with chiral surface through molecular reprinting with chiral ligands. Avnir et 35 al [5] were to our knowledge first todemonstrate this possibility for metal particles in 2009. Gun'ko et al have shown that using amino acid ligands it is possible to create chiral nanoparticles showing the circular dichroism spectra typical of chiral molecular objects after complete removal of templating ligands for both 40 quantum dots[120] and oxide nanoparticles.[51] The same approach was applied later for creation of chiral oxide nanostructures imprinting them from chiral protein template.[121]

Control of porosity

Mesoporosity

45 Many industrial applications of metal oxides such as in catalysis, photocatalysis, in the electrodes of solar cells and in alkaline metal ion batteries require materials with well-defined and highly uniform mesoporosity. The nucleation mechanisms in Soft Chemistry syntheses are thus very advantageous rendering 50 nanoparticles in the meso-size scale, i.e. in the nm scale. The challenge lies in letting them aggregate without closing of the pores on the surface – a typical drawback of the common metal oxide sol-gel. A solution based on prolonged high temperature solvothermal synthesis[61] is quite energy demanding and is 55 difficult to realize on larger scale. It has to be mentioned that in the solvents containing water, for example, ethylene glycol, diethyeleneglycol, PEG etc. the long term hydrothermal treatment

generates bubbles of water vapor initiating self-assembly of generated nanoparticles on their surface leading to formation of 60 mesoporous spheres.[122,123] The conditions for these cases are generally milder than for the syntheses in benzyl alcohol and the removal of the residual organics is more facile, but still the energy and time consumption and productivity remain a concern for these techniques.

65 Two principal strategies have been proposed to facilitate formation of open porosity from the primary nanoparticles: one based on application of amphiphilic ligands and the other – on using solid easily hydrolysable precursors with volatile ligands. The idea in application of amphiphilic ligands lies in their easy 70 solubility in both water and in non-polar organic solvents. The approach exploits the same principle as that behind the common "inorganic garden experiment",[124] i.e. generation of semipermeable membrane coated vesicles that explode under osmotic pressure. The experiment is organized in the way that a 75 hydrocarbon solution of an alkoxide precursor, modified with amphiphilic organic ligand, is sprayed into water. Its mechanism is explained in Fig 12.[125]
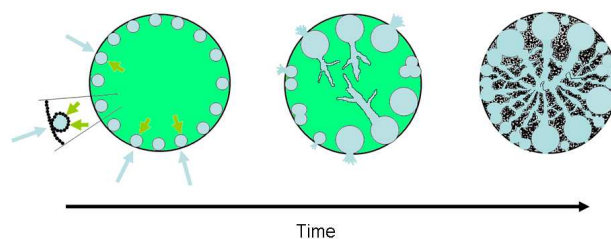

Figure 12. Mechanism of formation of a hierarchically porous TiO_2 80 sphere on spraying a toluene solution of $[Ti(OR)_3Pc]_2$ into water, where Pc is the anion of amino acid penicyllamine. Reprinted with permission from [125].

When a droplet of alkoxide solution gets into water is is immediately covered by a continuous layer of coalesced primary 85 nanoparticles. The diffusion of water through this thin oxide membrane leads to formation of water droplets on the inside of it. The droplets are in their turn covered by a new membrane of coalesced particles. Both water from outside and the amphiphilic ligands from inside diffuse inside the thus formed vesicles 90 creating increased osmotic pressure. Finally, the vesicles explode. If they do this into outside the vesicle gets an opening to the surroundings. If the explosion goes inside, a protuberance of aqueous solution comes into contact with the solution of precursor and gets coated with a new membrane forming a new 95 bigger vesicle that later explodes in its turn etc. As the result a structure with macro pores from vesicles and meso pores from the structure of the emerging membranes of coalesced primary particles is formed resulting in creation of hierarchically porous spheres. This approach can potentially be up-scaled to give high 100 yields of particles with open hierarchical porosity.

Keeping essentially solely mesoporosity, originating from coalescence of the primary particles, oxide phase nuclei, which are completely insoluble in the media, is possible when their formation occurs through transformation of a crystal of solid 105 metal alkoxide immersed into boiling water. It is important in this case that the precursor does not contain stable to hydrolysis amphiphilic ligands. Presence of the latter as it has been shown by Daniele et al. results in separation of the emerging particles

and formation of a stable colloid built up of the surface-capped oxide crystals.[95,96] An interesting feature is that the transformation involves at an intermediate step formation of a truly ordered (commonly lamellar) mesoporous structure, which is mostly amorphous. The origin of the latter is presumably the diffusion controlled hydrolysis-condensation resulting in densification of the precursor crystal along existing crystallographic directions with formation of oxide (see Fig. 13).[97]
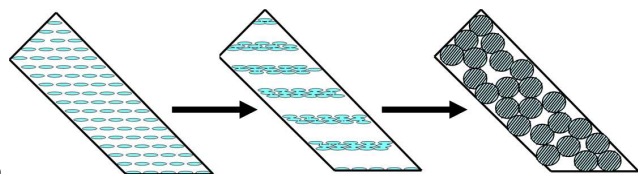
Figure 13. Hydrolysis-condensation in an alkoxide precursor crystal leading to emergence of intermediate ordered mesoporous structure. Reprinted with permission from.[97]

Boiling of the produced structure in water for just half-an-hour results in fully crystalline material, where the primary crystalline particles are already formed and distributed through the volume of the original precursor crystal in an essentially random manner. Their uniform size and random distribution result in a thermally relatively stable open mesoporous structure.[97] This material turned out to be very useful as adsorbent or substrate for hybrid adsorbents,[97] but even as electrode material for Li-insertion in Li-ion batteries.[126]

Building up a hierarchical macroporous-mesoporous structure is possible not only through solution techniques. In the cases where the crystal structure of a metal-organic precursor can influence its thermal decomposition geometrically, e.g. through release of solvating molecules on evaporation, there emerges a possibility to create macro pores by contraction of the crystal and mesopores through nucleation of the oxide phase on thermal decomposition. Recently, a number of attempts to create by this approach, for example, novel catalysts have been reported, in particular for $NaTaO_3$ – a perspective material for photocatalysis.[127]

Microporosity

The profound difference in chemistry between silica and metal oxides is manifested especially clearly in the difficulties associated with the synthesis of metal oxide membranes with reproducible microporosity. While silica independently of preparation route almost always reveals some microporosity, preparation of microporous metal oxides is a considerable challenge. The reason lies quite understandably in the profound mechanistic difference in formation of these phases. While silica results from inorganic polymerization reactions with no distinct preference for, in particular, the size of O-Si-O-Si rings in the structure, which then is inherently microporous, the metal oxides emerge through nucleation in the form of dense polyoxometallate structure particles with the size in the nm scale. Metal oxides thus reveal mesoporosity and essentially absence of microporosity. It is worth noting that organic ligands resistant to hydrolysis such as residues of chelating organic acids would be able to give rise to micropores on subsequent thermal treatment if they remained inside the structure of the primary particles and were not moved out to the surface of the particle as chelating ligands usually do.

Solution to this problem was found in application of simultaneously chelating and bridging ligands. When precursors bearing these ligands are used in sol-gel processing in not extremely acidic media (so that the ligands are not completely protonated and desorbed), the ligands remain in the structure of the forming particles less crystalline in this case, and leave micropores when removed on subsequent thermal treatment. An example is successful application of the $Zr(dea)_3Ti_2(O^iPr)_6$ precursor (where dea is the deprotonated residue of diethanolamine, H_2dea). Zirconium titanate $ZrTi_2O_6$ films produced from this precursor displayed reproducible microporosity with the pore size about 8 Å (0.8 nm) and were successfully used when deposited onto macroporous alumina substrate as gas-separation membranes in purification of raw oil.[128]

Control of chemical composition in complex systems

The idea to achieve and maintain the chemical composition in the desired material through precursor chemistry represented the main focus in precursor research for really long time. It has been denoted generally as "single-source precursor" (SSP) approach, but both target materials and techniques used for its implementation have been historically quite diverse.

Historically the idea to apply a single precursor compound first came up, as far as authors could find, in MOD as a response to challenges in preparation of high purity single phase $BaTiO_3$ ferroelectric for capacitor applications. The compound with tentative formula $BaTiO(C_2O_4)_2 \cdot 4H_2O$ was isolated and successfully applied for production of high purity $BaTiO_3$ by thermal treatment. The unified procedure has been reported by the US national bureau of standards as early as in 1956.[129] The molecular and crystal structure of the precursor was reported in 1992 showing it to be $Ba_4Ti_4O_4(C_2O_4)_8 \cdot 20H_2O$. The (nano) crystalline $BaTiO_3$ was shown to be product of its thermal decomposition at 900°C.[130]

The challenge that specifically intensified the development of SSP lied in MOCVD in connection with the aim to develop high quality gallium arsenide films for new generation of computer chips in the 1980-es. Volatile heteroelement species such as, for example, $Me_2Ga(\mu-^tBu)_2As$, have been successfully prepared and characterized, but producing a film with proper Ga : As = 1:1 stoichiometry remained a considerable challenge – the GaAs films obtained with SSPs were often Ga deficient.[131]

Very soon with the growing interest to films of ferro- and piezoelectric materials and especially with the discovery of High Temperature Superconductors (HTSC) the major effort in development of SSP moved into the domain of sol-gel. Alkoxides were identified as most attractive class of compounds. The search for suitable precursors was originally run as systematic studies of solution equilibria in double alkoxide systems and turned successful for use in the synthesis of especially ferroelectrics. The compounds with formula $BaTiO(O^iPr)_4(^iPrOH)$, stable in solid phase, but unstable in solution,[132] and the solution stable $BaTiO(O^nBu)_4(^nBuOH)$[133] were identified and characterized in the studies led by By Turova and Yanovskaya et al.[134] The latter precursor was successfully applied commercially in the sol-gel synthesis of high quality $BaTiO_3$ films by Symetrix Corp. Colorado. In developing approaches to piezoelectric materials a principal achievement was made by Hubert-Pfalzgraf et al. in

application of alkoxide carboxylate precursors. [135] An important class of compounds, acetate-iso-propoxides of divalent elements and niobium, $M(II)(OAc)_2Nb_2(O^iPr)_{10}$, M(II) = Mg, Zn, Cd, for production of barium magno-niobate material, $BaMg_{1/3}Nb_{2/3}O_3$, was prepared and characterized. [136] Less well the things were developing with approaches to HTSC. The alkoxides, quite useful in preparation of films due to generally high viscosity and extremely good adhesion for colloids produced from them, were in this case apparently unable to lead to formation of proper complex oxide phase. The major hinder was the fact that HTSC phases are generally not thermodynamically stable at room temperature. Their formation occurs at high temperatures and requires specific oxygen stoichiometry. The Soft Chemistry is leading to nucleation of materials in a coordination equilibrium type processes, so only stable phases can be formed with advantage using these approaches. Today it is possible distinctly to say that simple perovskites and spinels can successfully be accessed by alkoxide-based sol-gel synthesis and in some cases in a more advantageous way by using single-source precursors.

Relatively large scale and considerable cost sensitivity for sol-gel technology urged the search for reliable design concepts and development of new simple and reproducible techniques for synthesis of complex precursors. The ground principles for design of the structures of metal alkoxides were laid down by the analysis of the molecular structure types for metal alkoxides provided in the first comprehensive review of heterometallic alkoxide complexes by Caulton and Hubert-Pfalzgraf. [137] A crystallographic Molecular Structure Design Concept based on Goldschmidt's principles for inorganic structure construction has been developed in early 2000-es, [138] permitting to predict the existence and identify efficient synthetic pathways to over hundred new potentially attractive precursors. The idea in its background is that for a desired metal cation combination it should be possible to choose an appropriate structure type that can be completed by ligands providing both the required number of donor atoms and the necessary sterical protection of the chosen metal cation – donor atom core. The compounds that could be proposed belonged to such classes as oxoalkoxides, [139-142] alkoxide beta-diketonates, [37,41,143-149] alkoxide carboxylates [150,151] and functional alkoxides (derivatives of amino alcohols, alkanolamines etc.). [89,152-155] About two hundred individual compounds have been purposefully synthesized and structurally characterized.

The synthetic approaches can be considerably simplified with understanding that metal alkoxides and related species are based on ionic bonding and thus can be constructed using self-assembly approach, i.e. combining metal cations with the chosen ligands in a one-pot self-assembly synthesis. [138] It is important to keep in mind that ligands can have direct effects even on the pH in the further sol-gel processing. For example, chloride ligands generate hydrogen chloride, HCl, on hydrolysis, i.e. acidic medium, while bimetallic alkoxides with alkali and alkali earth metals and amino alcohols give rise to basic media. [116,117] The pH of solution influences possible redox reaction pathways if the cations can adopt different oxidation states.

The SSP approach today is specifically interesting for application in solvothermal techniques, which are actively exploited in preparation of, for example, rare earth element doped oxide or

fluoride nanoparticles for bio-imaging. Using molecules with analogous structure and stability it is possible to achieve homogeneity of doping at the molecular level. Cubic, like $BaTiO_3$, [91] and hexagonal, like $LaAlO_3$, [46,156] oxide perovskites and hexagonal $NaYF_4$ [157] bimetallic fluorides are among the most investigated ones.

Considerable focus during the last decade was set also on the development of single-source approaches to simple and complex chalcogenides. The process is thermodynamically controlled, which permits to design synthetic pathways to rather complex selenide and telluride phases via, for example, use of seleno- or telluro phosphines. [158-161] Principal contributions to this particular area have been made by Paul O´Brien et al. [10]

The challenge in keeping the control over composition is especially complicated for MOCVD and ALD systems. A feature that through the years attracted very much attention in the synthesis of high-k dielectric oxides, extremely important for electronic industry, is minimization of the residual carbon content. Carbon impurities can in practice deteriorate the dielectric properties of the desired oxide phase produced especially by MOCVD technique. An idea to introduce specific ligands decreasing the temperature of thermal decomposition in the deposition processes, [162] for example, by introduction of hydride ligand in the precursor structure bearing branched alkoxide ligands such as t-butoxide, turned in reality unsuccessful: the reaction mechanisms are not really molecular – the emerging nuclei of oxide get reduced and initiate polymerization and carbonization of the organic ligands (compare RAPET, [80-83]). Much more fruitful approach turned to be introduction of more thermally stable ligands requiring increase in deposition temperatures and permitting to avoid carbonization. This approach has been pioneered and propagated by A.C. Jones et al. who proposed to use alkoxide beta-diketonate complexes [163] and also amino alkoxide modified alkoxides. [164,165] Many successfully applied heterometallic species of this kind have been used to produce carbon-free perovskite coatings of $MTiO_3$ and $MZrO_3$, where M = Ba, Sr. [166,167] Heterometallic precursors have potential to provide solution in coating complex surfaces.

Even higher stability and more efficient decomposition into oxides were observed for alkoxide beta-ketoesterate compounds proposed by A. Devi et al. [168-170] Recently attempted application of homometallic alkyl alkoxides as precursors turned unsuccessful with rather low growth rate. The reasons of these difficulties have been explained using the data of theoretical calculations and mass-spectrometric analysis of the gas phase. [171] Some studies of heterometallic alkyl alkoxides that appear interesting from coordination chemistry point of view have also been reported. [172] Strong focus in attempts to improve the quality of MOCVD high-k films has recently been set on application of N-donor ligand derivatives (amides, guanidinates etc.) of M(IV) – they are formed as in situ nitrogen-doped materials and avoid carbon contamination while displaying better crystallinity. [173]

Concluding remarks

The over 50 years old chemistry of molecular precursors remains clearly a strong knowledge and inspiration source for development of the modern field of nanomaterials constantly offering new more and more efficient and attractive approaches to

systems with controlled composition and functional characteristics including morphology, porosity and chemical reactivity. The mechanistic features of these processes are now proved to be common for all Soft Chemistry approaches and involve the step of nucleation, growth or, alternatively, oriented attachment, and, finally, phase separation or formation of a continuous nanosystem.

Acknowledgments

Notes and references

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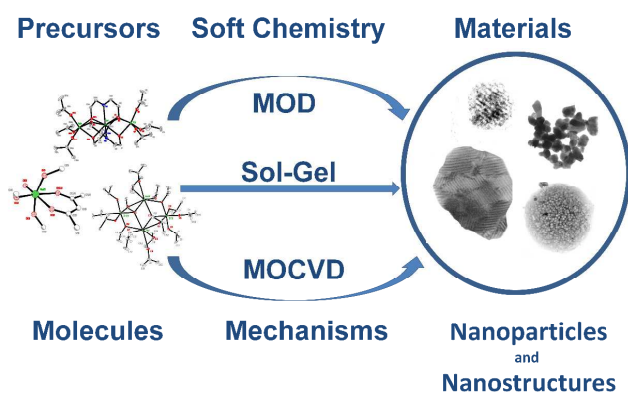[b] *CaptiGel AB, Uppsala Science Park, 75183 Uppsala, Sweden*

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TOC graphic

The review summarizes basic principles in the mechanisms of Soft Chemistry synthesis giving access to nanoparticles and nanostructures with controlled architecture, morphology and composition.