

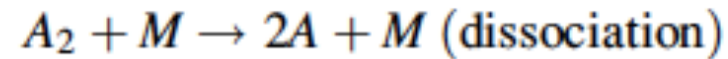
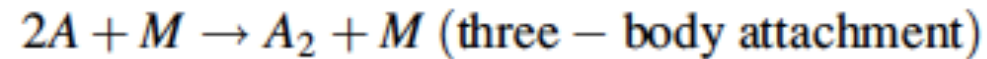
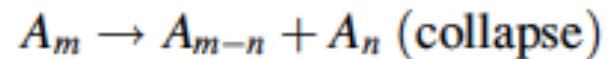
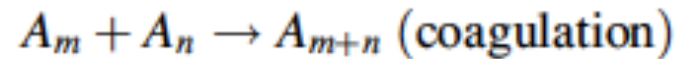
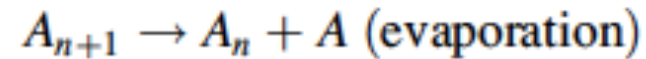
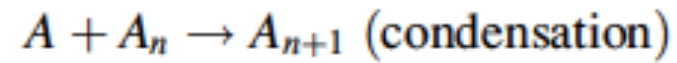
Synthesis of Nanomaterials

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2. Synthesis Mechanism

The possible pathway for the generation and growth of atomic clusters.

The symbol A represents a mono-atomic molecule or a monomer, A_n is a cluster consisting of n -monomers (referred to as an “ n -cluster”), and M is a molecule of a carrier gas.



Hybrid methods of preparation seek to combine both physical and chemical methods to produce NPs.

In these methods, the ability of physical methods to produce monodisperse nanocrystals is coupled with the ease of chemical synthesis to overcome the barrier of low throughput of physical processes.²

Solvated Metal Atom Dispersion (SMAD)

The SMAD method relies on trapping metal atoms in a cold matrix formed by a condensed liquid, followed by a growth step that occurs when the matrix is warmed to room temperature.

By controlling factors such as **solvent polarity** and the **rate of heating**, the size of the nanocrystals can be tuned.

The reaction is carried out in a vacuum chamber filled with liquid vapors. The walls of the chamber are cooled to liquid nitrogen temperature and the metal atoms are introduced by thermally evaporating a metal chunk.

The atoms upon evaporation get embedded in the solvent matrix condensed on the walls.

Klabunde and coworkers have adapted this method to synthesize Au nanocrystals in gram scale.

They have modified the SMAD scheme to include alkanethiol in the cold matrix and obtained monodisperse nanocrystals following a size fractionation method.

Seed-Mediated Growth

The seed-mediated growth is the most apparent approach for the separation of nucleation and growth.

Nucleation is physically separated from growth by using preformed nanocrystals as seed nuclei, i.e., heterogeneous nucleation prevents the formation of additional nuclei by homogeneous nucleation.

Preformed nuclei in the reaction solution are supplied with monomers that react on the surface of the nuclei.

It is important that the monomer concentration is low enough to suppress homogeneous nucleation.

Seed-mediated growth can be divided into two categories related to homogeneous and heterogeneous particles.

Homogeneous particles consist of just one material, whereas heterogeneous particles have compositionally different sections, e.g. in core-shell structures.

Seed-mediated growth has mainly been developed for the synthesis of metallic NPs, and metal oxides, in particular for magnetic NPs.

It is possible to achieve exceptionally narrow size distributions (standard deviation $\sigma < 5\%$), if the seed nuclei are also very uniform.

An impressive example along these lines is the preparation of iron oxide nanocrystals, whose diameter can be adjusted in one nanometer increments. The synthesis involves a two-step process.

Firstly, monodisperse iron NPs were prepared from iron pentacarbonyl $\text{Fe}(\text{CO})_5$ and oleic acid in dioctyl ether. Depending on the molar $\text{Fe}(\text{CO})_5$ -to-oleic acid ratio the size of the iron NPs can be adjusted from 4 to 8 and 11 nm.

A very subtle size-tuning in one nanometer increments is then possible by reacting these seed NPs with iron oleate solutions of defined concentrations, yielding monodisperse iron NPs that transform into iron oxide NPs of 6, 7, 8, 9, 10, 11, 12, and 13 nm on exposure to air.

The small size distribution leads to a hexagonally ordered arrangement of the NPs.

Surfactant-Directed vs. Solvent-Controlled Nonaqueous Sol-Gel Approaches

Nonaqueous processes can roughly be divided into surfactant- and solvent-controlled approaches.

(i) Surfactant-controlled synthesis routes involve the transformation of the precursor species into the oxidic compound in the presence of stabilizing ligands in a typical temperature range of 250 to 350 °C.

The most popular and successful approach within this strategy is the **hot injection method**, where the reagents are injected into a hot surfactant solution, which was particularly successfully applied in the synthesis of semiconductor nanocrystals.

(ii) An alternative is the use of common organic solvents, which act as reactant as well as control agent for particle growth, enabling the synthesis of high-purity NPs in surfactant-free medium.

In comparison to the synthesis of metal oxides in the presence of surfactants, the solvent-controlled approaches are simpler, because the initial reaction mixture just consists of two components, the metal oxide precursor(s) and a common organic solvent. The small number of reactants simplifies the characterization of the final reaction solution.

The synthesis temperature is typically in the range of 50 to 200 °C, which is notably lower than in the hot-injection method.

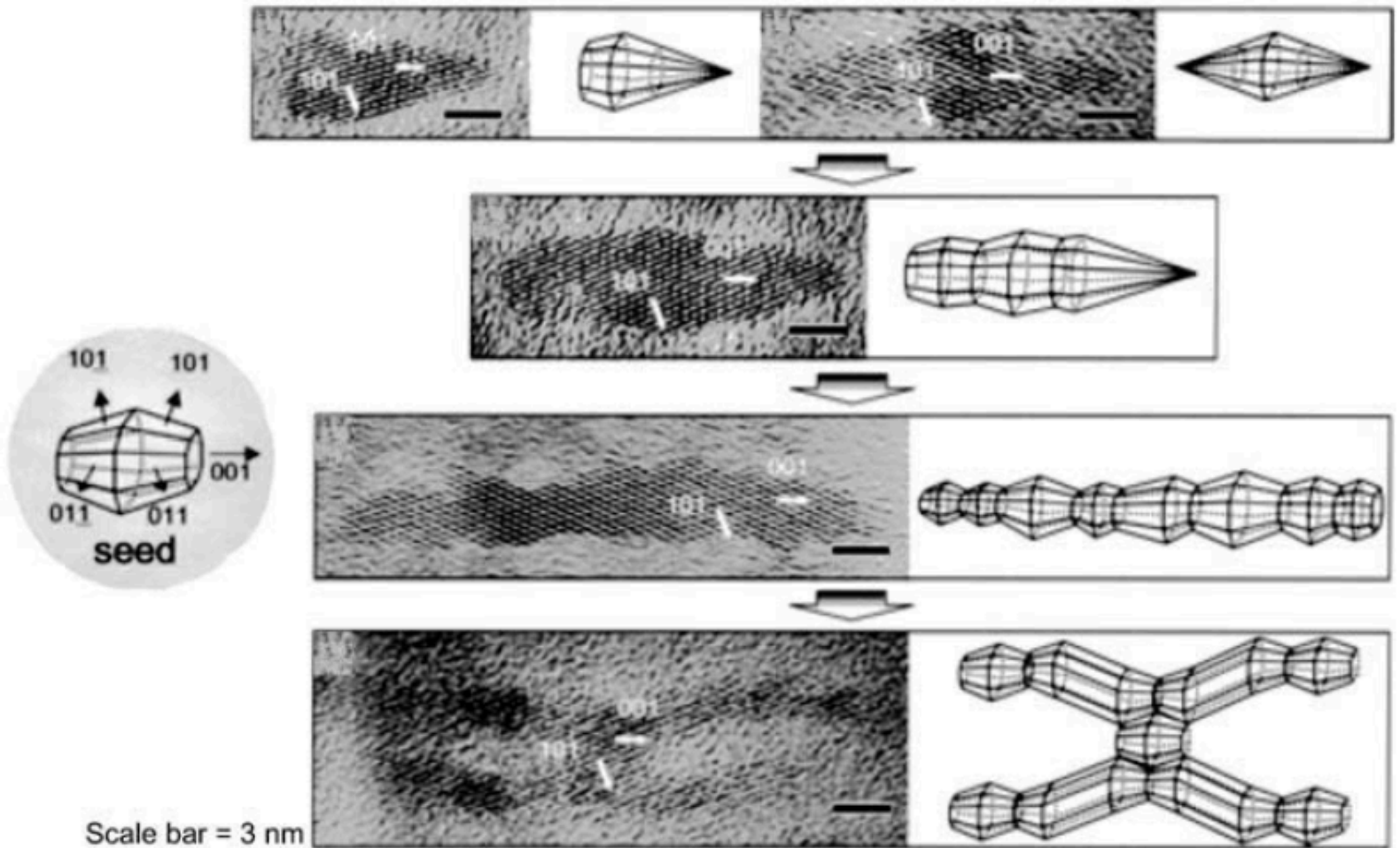
A comparison on both approaches clearly shows that surfactant routes permit outstanding control over the growth of metal oxide NPs, leading to almost perfectly monodisperse samples.

The ability of surfactants to cap the surface of the NPs, sometimes combined with selectivity towards specific crystal faces (Using **surface-selective surfactant** e.g. lauric acid), provides advantages such as shape control, low agglomeration tendency, good dispersibility in organic solvents, and the potential to tailor the surface properties.

Depending on the **surface-selective surfactant** concentration, the shape of the anatase nanocrystals varies from bullet- and diamond-like to rods and branched rods.

Drawbacks resulting from surface-adsorbed surfactants are the unpredictable influence on the toxicity of the NPs, and the diminished accessibility of the particle surface, which is a serious issue regarding applications in gas sensing or catalysis.

Although solvent-controlled approaches generally result in some agglomeration, the dispersibility properties of the NPs can be improved by a post-synthetic functionalization step. In some cases a tiny amount of surfactants suffices to lead to completely transparent NP dispersions.



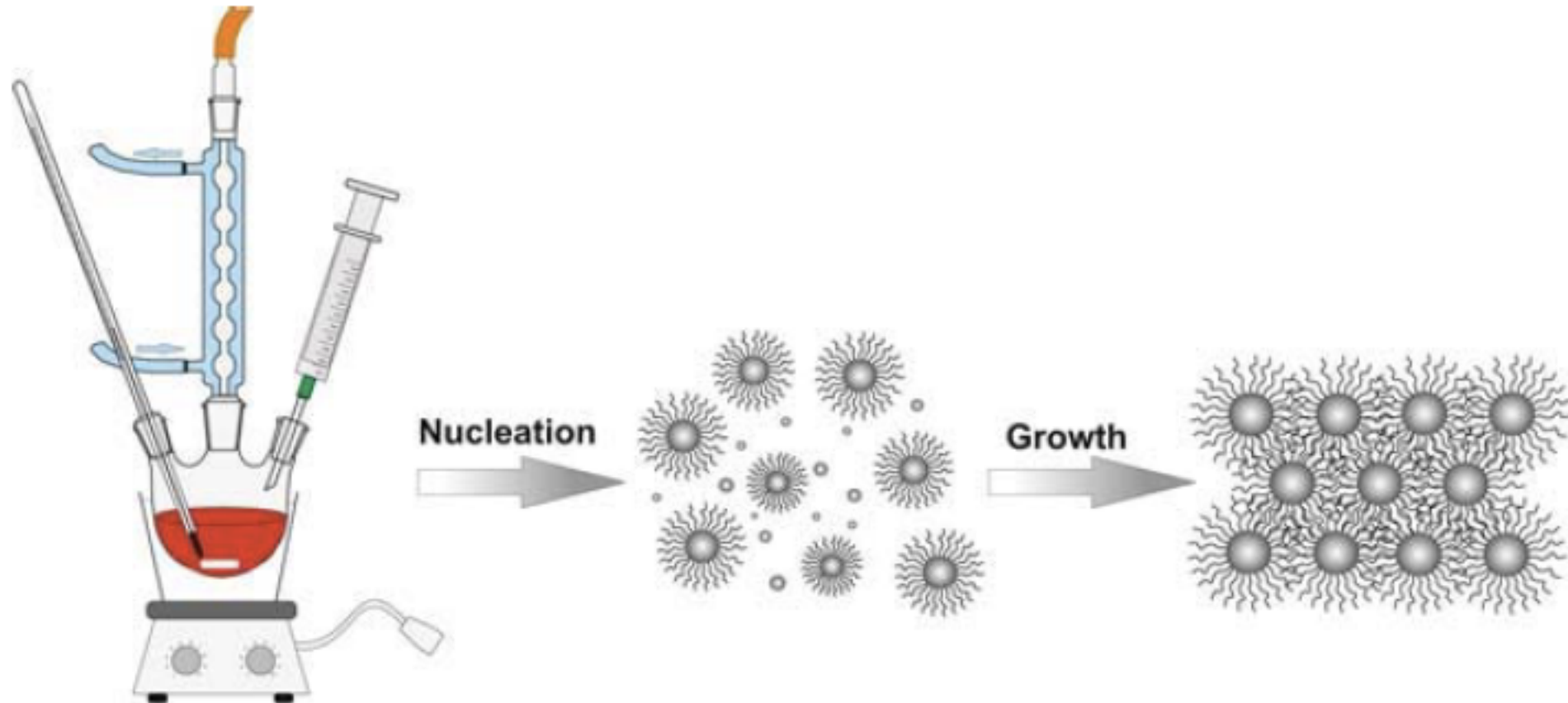
HRTEM images and simulated 3-D shapes (bullet, diamond, short rod, long rod, and branched rod) 8

Surfactant-directed approaches	Solvent-controlled approaches
Pros	
<ul style="list-style-type: none"> ● Excellent control over crystal size ● Narrow size distribution ● Good control over crystal shape ● Low agglomeration tendency ● Good redispersibility 	<ul style="list-style-type: none"> ● Low amount of organic impurities ● Non-toxic solvents ● Simple, robust and widely applicable synthesis protocols ● Good accessibility of the nanoparticle surface
Cons	
<ul style="list-style-type: none"> ● Large amount of organic impurities ● Toxicity of surfactants ● Restricted accessibility of the nanoparticle surface ● Complex reaction mixtures 	<ul style="list-style-type: none"> ● Less control over crystallite size and shape ● Broader size distributions ● Formation of agglomerates ● Restricted redispersibility

Surfactant-assisted Synthesis

Hot-Injection Method

In 1993, Murray et al. published the synthesis of monodisperse CdX (X=S, Se, Te) nanocrystallites in molten trioctylphosphine oxide (TOPO). This work provided the basis for the so-called hot-injection method, which involves the injection of a room-temperature (“cold”) solution of precursor molecules into a hot solvent in the presence of surfactants.



The fast injection of the precursor induces a high degree of supersaturation, resulting in a short burst of nucleation. During the nucleation process the precursor concentration in the solution decreases abruptly.

The drop in temperature, due to the injection of the “cold” reactants, and the low concentration of unreacted remaining precursor prevent any further nucleation events.

In a next step, the temperature is carefully increased to a value which allows the slow growth of the nuclei to larger NPs, however still suppresses further nucleation. The **separation of nucleation and growth** is a prerequisite to synthesizing monodispersed NPs, and therefore the hot-injection method generally leads to NPs with a narrow size distribution of $\sigma \sim 10\%$. If size distributions narrower than 5% are required, then a size-selection process has to be applied.

The surfactants, typically consisting of a coordinating head group and a long alkyl chain, adsorb reversibly to the surfaces of the growing NPs, and thus provide a dynamic organic capping layer that stabilizes the NPs in solution and also mediates their growth.

The use of surfactants with selectivity towards specific crystal faces, or mixtures of surfactants with different binding affinities to the nanocrystal surface allow excellent control over crystal size, size distribution and morphology.

Finally, the nanocrystals can be precipitated by adding a nonsolvent.

After their separation from the reaction liquid, the NPs can be redispersed in suitable, usually apolar, organic solvents, forming stable colloidal suspensions.

The surfactants used during the synthesis and now attached to the surface of the nanocrystals can be exchanged against other ones in a post-synthetic step, allowing not only the chemical modification of the surface properties of the NPs in general, but also the tailoring of the dispersibility behavior in different solvents in particular.

The hot-injection method proved to be particularly versatile for preparing II-VI, IV-VI and III-V semiconductor nanocrystals, however, it has also been extended to the synthesis of other materials such as metals, metal oxides and bimetallic oxides.

In addition to the injection of molecular precursors, also the rapid addition of metal oxide sols, amorphous nanoparticulate precursors, or reactive solvents to the hot solvent was reported as interesting modifications of the “standard” hot-injection method.

Heating-Up Method

In the so-called “heating-up” method the reaction solution is prepared at low temperature. Subsequent heating initiates the crystallization process, which finally leads to the formation of nanocrystals.

The heating-up method is particularly advantageous for large-scale production, because of its simplicity. Nevertheless, the size uniformity that can be achieved by this approach is comparable to the best results obtained from the hot-injection method.

Regarding the nucleation process, the main difference between the heating-up and the hot-injection method is the instantaneous supersaturation that is induced in the hot-injection method.

Although the crystallization mechanisms underlying the control of the size distribution in the heating-up method are much less understood than in the hot-injection method, one would expect **different growth kinetics** for both methods.

Investigations in this direction did not yet show any significant differences, at least in comparison with other, obviously more important reaction parameters.

Solvent-Controlled Synthesis

The use of coordinating organic solvents represents an alternative to surfactants, especially in cases where the accessibility of the particle surface as well as the amount of organic impurities are important parameters.

In comparison to the synthesis of metal oxides in the presence of surfactants, the solvent-controlled approaches are on the one hand considerably simpler (the starting reaction mixture generally just consists of a metal oxide precursor and a common organic solvent), and on the other hand the synthesis temperature is lower, typically in the range of 50 to 200 °C.

The main advantage of surfactant-free synthesis methods lies in the improvement of product purity. Surface-adsorbed surfactants not only influence the toxicity of NPs, but also lower the accessibility of the NP surface in catalytic and sensing applications. These problems are circumvented in nanopowders obtained by surfactant-free routes.

In the solvent-directed approaches the organic solvent can act as reactant as well as control agent for particle growth.

However, the detailed role of the organic species in these approaches is rather complex. On the one hand they provide the oxygen for the formation of the metal oxide, and on the other hand they act as capping agent, which binds to the particle surface, and thus limits the particle growth, and influences morphology and assembly behavior.

The complexity arises from the fact that many organic species may be present in the final synthesis mixture. In addition to the excess of organic solvent and the unreacted organic part of the precursor molecules, also various other organic condensation products are formed as a result of chemical reactions between these organic species.

If the temperature is well below the boiling point of the organic solvent, then a standard laboratory oil bath on a hot plate combined with stirrer is the easiest option. This set-up is also suitable for experiments under reflux conditions.

If higher temperatures, i.e., close or above the boiling points are required, then autoclaves represent the containers of choice. For the production of NPs on a laboratory scale, i.e., 0.1–1 g, typically Parr acid digestion bombs with 45 mL Teflon cups are employed. The Teflon liners provide protection against corrosion.

The porosity of the Teflon leads to contamination with NPs, which means that every Teflon cup should only be used for one material. In some selected cases, the role of the autoclave is not only to provide solvothermal conditions or high reaction temperatures, but also to prevent the evaporation of low-boiling organic compounds that need to be present in the reaction vessel to drive NP formation to completion.

For a larger scale, it is possible to use 1 L autoclaves that offer, in contrast to the smaller ones, mechanical stirring for the homogenization of the reaction mixture. Using this reactor size, it is possible to get metal oxide nanopowders in the range of 20–50 g per batch.

Modern commercial microwave ovens provide the possibility to stir the reaction mixture, control the temperature and power applied, all of which improve the reproducibility of the synthesis protocol. This set-up allows a homogeneous penetration of the microwave irradiation into the reaction vessel under precise control of temperature and pressure.

Rapid cooling can be performed by means of a compressed air jet, so that the reaction can be efficiently thermally quenched.

The short reaction times ranging from 30 seconds to 3 minutes make it possible to prepare a large number of batches within a short time, thus giving access to large quantities of inorganic NPs.

References

Niederberger, M., Pinna, N.; *Metal Oxide Nanoparticles in Organic Solvents*; Springer-Verlag: London, 2009.

Aliofkhazraei, M. (Editor); *Handbook of Nanoparticles*; Springer: Switzerland, 2016.