

# Multifunctional, Hybrid Materials Design via Spray-Drying: Much more than Just Drying

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Spray-drying is a popular and well-known “drying tool” for engineers. This perspective highlights that, beyond this application, spray-drying is a very interesting and powerful tool for materials chemists to enable the design of multifunctional and hybrid materials. Upon spray-drying, the confined space of a liquid droplet is narrowed down, and its ingredients are forced together upon “falling dry.” As detailed in this article, this enables the following material formation strategies either individually or even in combination: nanoparticles and/or molecules can be assembled; precipitation reactions as well as chemical syntheses can be performed; and templated materials can be designed. Beyond this, fragile moieties can be processed, or “precursor materials” be prepared. Post-treatment of spray-dried objects eventually enables the next level in the design of complex materials. Using spray-drying to design (particulate) materials comes with many advantages—but also with many challenges—all of which are outlined here. It is believed that multifunctional, hybrid materials, made via spray-drying, enable very unique property combinations that are particularly highly promising in myriad applications—of which catalysis, diagnostics, purification, storage, and information are highlighted.

## 1. Introduction

If a strawberry has a wonderful taste and a kiwi has one as well, how would a fruit hybrid of both taste

This thought translated to the nano and the molecular world would mean: If nanoparticles and molecules alone possess fantastic properties, what would properties look like after a merge

Up to today, scientists have mastered designing nanoparticles in all kinds of compositions, sizes, and structures and they have established myriads of highly functional molecules. Now, we have all these moieties as building blocks at hand to develop more complex entities. The upcoming century will be the century of the next hierarchical level, where we will look at what objects and properties can be obtained upon joining nano and molecular building blocks. To achieve this, many different strategies are at hand, for

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DOI: 10.1002/adma.202306648

instance, self-limited self-assembly,<sup>[1]</sup> or assembly through specific molecular, e.g., DNA-based, protein-based, interactions.<sup>[2]</sup> Many approaches require highly controlled and tailored chemistry and are often only successful in specific cases.

An alternative approach is to neglect to pay attention to chemical “preferences” or “affinities” and rather use “brute force” to join moieties. Such a brute force method is to put together the target moieties in a confined space and narrow down this space more and more until the moieties have no other option than to join as a new composite entity. A concrete way of doing this is via dispersing nano- or molecular building blocks in a dispersion liquid, then forming a droplet and ultimately evaporating the liquid. Techniques to realize such an approach include emulsion-based assembly (including microfluidic process-controlled emulsions, or surfactant-based as well as surfactant-free emulsions) or the droplet evaporation on a surface.<sup>[3]</sup>

Among these methods, spray-drying stands out as it is the most “chemistry-independent” and versatile approach, as it is simple, fast, amenable to continuous processing, as well as scalable and yields reproducible results.<sup>[4–7]</sup> In principle, any nano or molecular building blocks in dispersion are fed into a nozzle, which creates small droplets. These droplets are then dried in a hot chamber, resulting in typically micrometer-sized entities composed of the aforementioned building blocks, which are subsequently joined. This process is universally applicable as long as the chemical moieties are firstly dispersible/soluble in a liquid and secondly, the liquid can be evaporated before the moieties take off to the gas phase. These criteria are rather simple and can be fulfilled for most moieties and thus, in principle, make the process chemistry-independent. Moreover, as it is simple, it makes it also easily scalable and obviously, the process is fast, making it superior to many other assembly methods regarding the listed aspects. As the building blocks during spray-drying are by the process colocalized as an entity in time and space, this fact alone, or secondary effects such as coupling among the building blocks or the so-called “emergence,” yield new properties that could not be achieved with the individual building blocks alone.<sup>[8]</sup>

The ability to join building blocks with hardly having to pay attention to finely designing chemical affinities and the possibility to perform “chemistry in a droplet” upon the spray-drying event render this technique very powerful. In the field of pharmaceuticals/drug design<sup>[9]</sup> as well as foods,<sup>[10]</sup> spray-drying has been employed as a versatile tool for a long time already. Also, for basic chemical drying or impregnation operations, spray-drying is well-established and performed in the industry.<sup>[11]</sup> However, we believe that the enormous potential to design novel, multifunctional materials via spray-drying was unjustifiably neglected too much in the past by materials chemists. Our intention herein

is therefore to draw the attention of our fellow scientists to this technique.

From a fundamental science perspective, it is highly interesting to study the properties that result from the cooperative interplay of the (sometimes very different) building blocks that were joined by force and that would not have come together in any other way. But there is also a great application perspective: the powder of micrometer-sized entities can be easily handled and treated like standard additives and thus, upon its employment, equip materials with novel properties. Pushing it to the extremes, inside of such an entity an own ecosystem can be designed, e.g., to be a little microreactor on its own, thus acting as a highly interactive object.

Herein, we do not aim at reviewing spray-drying and its principles and achievements as such, as informative reviews on this do exist already.<sup>[4,12–14]</sup> Rather, we aim at giving a perspective on the future potential of obtaining multifunctional, hybrid and to date unthinkable materials upon employing spray-drying as a tool to assemble a plethora of building blocks by force.

## 2. Spray-Drying as a Highly Versatile Tool for Material Chemists

### 2.1. Material Formation via Spray-Drying

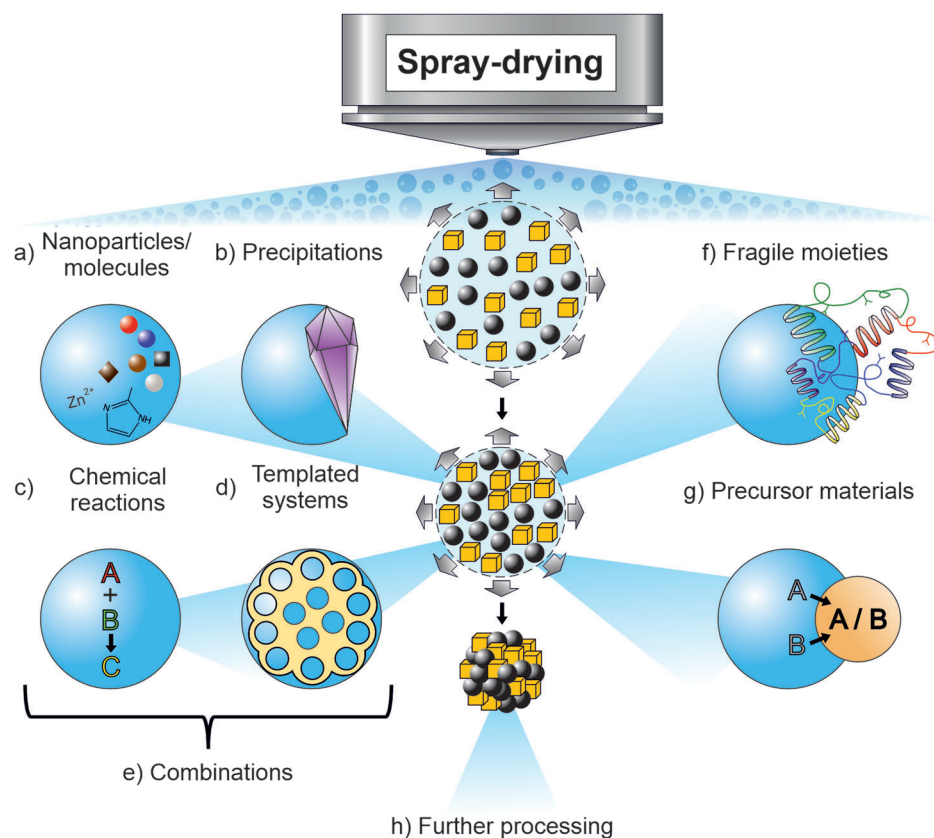
Upon spray-drying, the confined space of a liquid droplet is narrowed down and the liquid dispersion medium is dried (**Figure 1**). Although seemingly simple, this process can be exploited for a variety of material formation strategies: a) nanoparticles and/or molecules can be assembled; b) precipitation reactions can be performed; c) chemical syntheses/reactions are possible upon the drying event; d) templated materials can be designed; and of course, e) any combinations of (a) to (d) at the same time can be achieved. Beyond this, f) fragile moieties can be processed, or g) “precursor materials” can be prepared. h) Post-treatment of spray-dried material eventually enables the next level of material design.

Whenever nanoparticles are involved in the spray-drying process, as defined earlier,<sup>[8]</sup> we will denote the formed entities as “supraparticles” throughout this *Perspective* article.

#### 2.1.1. Nanoparticle and/or Molecule Assembly

The self-assembly of building blocks, such as nanoparticles and molecules within a single droplet upon solvent evaporation<sup>[8,15]</sup> can produce a variety of compositions (e.g., single-component,<sup>[16]</sup> multi-component,<sup>[17,18]</sup> inorganic-organic hybrid,<sup>[19]</sup> metal oxide hybrid<sup>[20,21]</sup>) and structures (e.g., solid,<sup>[22]</sup> hollow,<sup>[23]</sup> core-shell<sup>[23]</sup>) with unique properties and potential applications. Recently, many types of unique building blocks such as nanofibers,<sup>[24]</sup> nanorods,<sup>[25]</sup> and metal-organic frameworks (MOFs)<sup>[26,27]</sup> have become available and offer potential advantages. However, maintaining the distinct properties of the building blocks during self-assembly is highly important. To address this, researchers should aim to hybridize the material properties of building blocks with the features of the aggregate particles, leading to the development of new materials with unique

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**Figure 1.** Upon spray-drying the confined space of a liquid droplet is narrowed down and the liquid dispersion medium is dried. Using this principle, for instance, a) nanoparticles and/or molecules can be assembled, b,c) precipitations (b), or chemical reactions (c) can be performed, d) templated systems can be created, and e) any combination of (a–d) is possible. Beyond, f) fragile moieties can be processed or g) precursor materials can be synthesized. h) Post-treatment of spray-dried material eventually enables the next level of material design.

physical and chemical properties. Despite the potential of this approach, there are still several challenges that need to be addressed. One of the main challenges is achieving precise control of the particle structure, particularly when the assembly involves two or more different types of particles or molecules with different properties. To overcome this challenge, adjusting several factors such as process parameters (e.g., drying gas temperature, gas flow rate, nozzle configuration), physicochemical properties of nanoparticles (e.g., size, shape, density, surface potential, chemical composition, concentration, and mixing ratio in the case of multiple components), droplet properties (e.g., droplet size, surface tension, viscosity, boiling point, polarity), the drying rate of the solvent, and nanoparticle diffusion rate within droplets is essential.

### 2.1.2. Precipitation Reactions

One of the main virtues of spray-drying is that almost any solid-containing liquid can be processed. If at least one of the solids is initially dissolved in the feed, then solid formation by precipitation (also: nucleation) together with subsequent growth and agglomeration of the primary solids building blocks can be utilized for product design. Examples with nanoscale precipitates are the production of drug-loaded micro-

spheres (nanoscale drug particles to enhance bio-availability);<sup>[29]</sup> bimetallic nanoparticles for use in reduction and removal of chlorinated ethene and ethylene;<sup>[30]</sup> and molecular explosives (hexanitrohexaazaisowurtzitan).<sup>[31]</sup> By precipitation, the phase transition of the dissolved substance into a dispersed solid phase is achieved. The properties of the precipitated material depend on the thermodynamics and kinetics of the precipitation reactions.

In brief, precipitation reactions are triggered by a local or global excess in thermodynamic state variables, most commonly the solubility of the solid in the liquid phase. The corresponding solids concentration is a saturation concentration ( $c_s$ ) determined by thermodynamics; the local excess is typically expressed in terms of the supersaturation  $S = (c - c_s)$ . The kinetics of nucleation and further growth of the nuclei, e.g., into crystals, often follow a power law as a function of  $S$ , e.g.,  $S^g$  with a material-specific parameter  $g$ . For control of nucleation, e.g., to control the size and shape of the nuclei, it is of paramount importance to control the supersaturation or the underlying saturation concentration.

Supersaturation can be achieved along three routes, all of them manipulating the saturation concentration: 1) Controlled cooling: Solubility decreases with decreasing temperature. By controlled cooling of the feed during processing, the saturation temperature (concentration) is reached, and nucleation starts. In spray-drying, it is only of limited use as the feed (and droplet)

temperature is fixed by the adiabatic saturation temperature of the gas used in the spray-dryer. Only if the feed temperature is higher than the gas saturation temperature, control on supersaturation can be achieved. 2) Reduction of solvent volume: In spray-drying this is achieved by evaporation of the liquid. As solids volume remains constant, solids concentration increases to and beyond the saturation concentration and precipitation is initiated. As the liquid volume decreases further, a steady production rate of nuclei (with constant properties) can be maintained. The speed of evaporation can be manipulated by the gas-side conditions, allowing for a wide range of nucleation rates and nuclei properties. 3) Reaction-induced precipitation: The basis for this reaction type is that the reactants have a higher solubility than the reaction product.

New opportunities for material and product design can be achieved, e.g., by (ad-)mixing at least two reactants (e.g., by a droplet–droplet collision where one droplet is rich in component A and the other in component B). The reaction product is generated and then precipitates according to its level of supersaturation. The use of multiple immiscible fluid phases in one droplet with preferential precipitation of the components in one specific fluid phase presents a new opportunity over spatial arrangement of the components and the properties of the precipitates in the spray-dried particle. Thereby, complex structured patterns, like Turing patterns<sup>[28]</sup> or as generated by classical spinodal decomposition are imaginable, also in parallel with control of the domain sizes of the different components in the droplet and particle, respectively. Spatial patterning in general has been shown for molecular multiphase systems, e.g., acetone–water–malto dextrin solutions,<sup>[29]</sup> and is routinely applied in food engineering to protect nutrients from the environment.

### 2.1.3. Chemical Syntheses/Reactions

Spray-drying can become a very useful tool for the synthesis of new molecules and materials, as it is a fast, one-step, and reproducible process to mix reactants under well-controlled temperatures; can be performed under good manufacturing practices; can be easily scaled up; and the final product is a dry solid. With all these advantages, spray-drying has begun to be used for the efficient synthesis of not only a plethora of inorganic materials (e.g., oxides, ceramics, etc.), but also of molecular materials in which coordination, supramolecular and organic chemistry are involved. For all these syntheses, however, the inherent fast drying-kinetic nature of spray-drying can limit its use to perform reactions that require long reaction times. In these cases, implementation of these chemical reactions in spray-drying should require innovative solutions, such as the pre-treatment of the reactant mixture before its spray-drying using a continuous-flow reactor placed at the entrance of the spray-dryer.

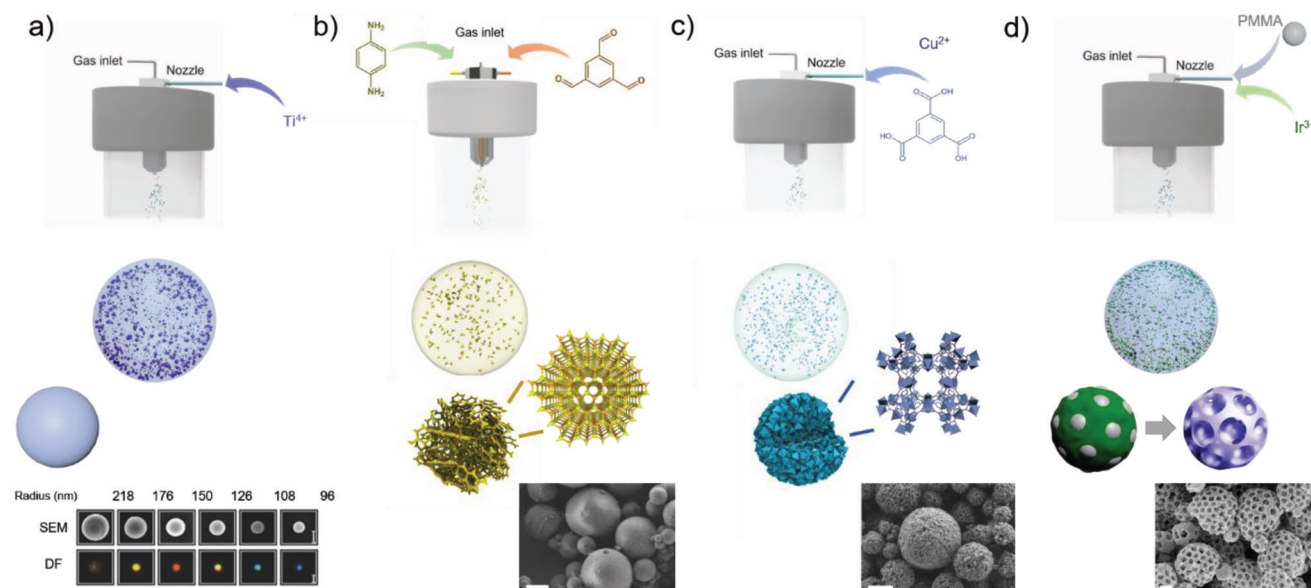
A clear example of a chemistry that can be performed in spray-drying is the sol–gel process, which enables the transformation of a molecular precursor into a metal oxo-macromolecular network or oxide nanoparticles based on inorganic polymerization reactions. This chemistry is thus ideally suited to prepare oxide spheres when coupled with spray-drying.<sup>[30]</sup> Typical precursors are metallo-organic compounds such as alkoxides, chelated alkoxides, or metallic salts such as metal chlorides, nitrates, sul-

fates, etc.<sup>[31,32]</sup> The typical reaction consists of two steps: 1) hydroxylation of metal precursors to form reactive hydroxy groups; and 2) polycondensation reactions (oxolation, ololation) through the formation of branched oligomers, inorganic polymers, and crystalline networks, typically after thermal annealing.<sup>[32]</sup> The nature of the inorganic network depends on the precursors, pH, water content, and aging. Indeed, the condensation degree of sol–gel-derived oxides evolves with time, the aging of the precursor solution is a key parameter affecting the properties and the nature of the final materials obtained by spray-drying. Spray-drying sol–gel systems requires a delicate control of the reactivity: one must design the process in order to minimize the condensation rate in the precursor solution before spraying and to trigger the condensation during drying. As mentioned above, long reaction times can represent a limitation. For instance, this issue can be overcome by using chemical additives in solution, inducing rapid modification of the pH during the evaporation, leading to condensation and oxide formation. Having these general considerations in mind, typical examples of spray-dried oxides spheres comprise conventional oxides, such as SiO<sub>2</sub>, TiO<sub>2</sub>, or ZrO<sub>2</sub>, and even multimetallic oxides, such as cobaltites or perovskites with exotic properties for applications in thermoelectricity, magnetoresistance and piezoelectricity.<sup>[33]</sup> Going beyond oxides, another way to obtain ceramic spheres, such as carbides, nitrides or boron-nitrides, involves the utilization of polymer-derived ceramics (PDCs).<sup>[34]</sup> Pre-ceramic polymers, such as polysilazane or polyvinylsilane, can be processed as polymers into micronic or nanometric spheres by spray-drying.<sup>[35]</sup> The cured pre-ceramic polymer can then be converted into ceramic material upon heating to a high temperature in an inert atmosphere, typically above 1000°C. During this pyrolysis step, the polymer undergoes a series of chemical reactions, such as decomposition, condensation, and crystallization, leading to the formation of ceramic materials.<sup>[34]</sup>

Going beyond traditional applications, among the emerging functionalities of spray-dried inorganic spheres, one of the most exciting directions is related to photonic metamaterials. Sub-micrometric sol–gel-based polycrystalline TiO<sub>2</sub> spheres obtained by spray-drying have been exploited as all-dielectric Mie resonators for a plethora of applications including vanishing back-scattering, enhanced directivity of a light emitter, beam steering, and large Purcell factors.<sup>[36]</sup> As shown in **Figure 2a**, those spherical nanoresonators possess a structural color that depends on their size and their dielectric properties that can be tuned taking advantage of the chemical versatility of spray-drying for fabricating complex metal oxides and including other optical functionalities. From a practical point of view, the spray-drying method coupled with inorganic polymerization will allow for a direct transformation of the precursors' solution in ready-to-use metamaterials to be sprayed on a surface or adapted for the production of meta-pigments or meta-paints.

Besides solgel reactions, the scope of chemistries accessible by spray-drying also includes coordination chemistries. In 2013, MasPOCH et al. first reported the use of spray-drying as a rapid, continuous method to synthesize MOFs,<sup>[37]</sup> which are organic-inorganic hybrid, crystalline, porous materials assembled from metal ions or clusters, and organic linker molecules. MOFs have shown promise for applications such as gas storage, catalysis, drug delivery, thermal energy storage, sensing, and





**Figure 2.** Schematic illustration of the synthetic versatility of spray-drying. a) Synthesis and SEM images of sol-gel derived  $\text{TiO}_2$  microsphere resonators (scale bars: 500 nm) (a); b) spherical beads of an imine-linked COF (Scale bar = 2  $\mu\text{m}$ ); c) MOF HKUST-1 (scale bar = 2  $\mu\text{m}$ ); and d) sol-gel derived porous metallic iridium microspheres (Scale bar = 200 nm). a inset) Adapted with permission.<sup>[36]</sup> Copyright 2018, John Wiley and Sons. d inset) Adapted with permission.<sup>[48]</sup> Copyright 2020, Royal Society of Chemistry.

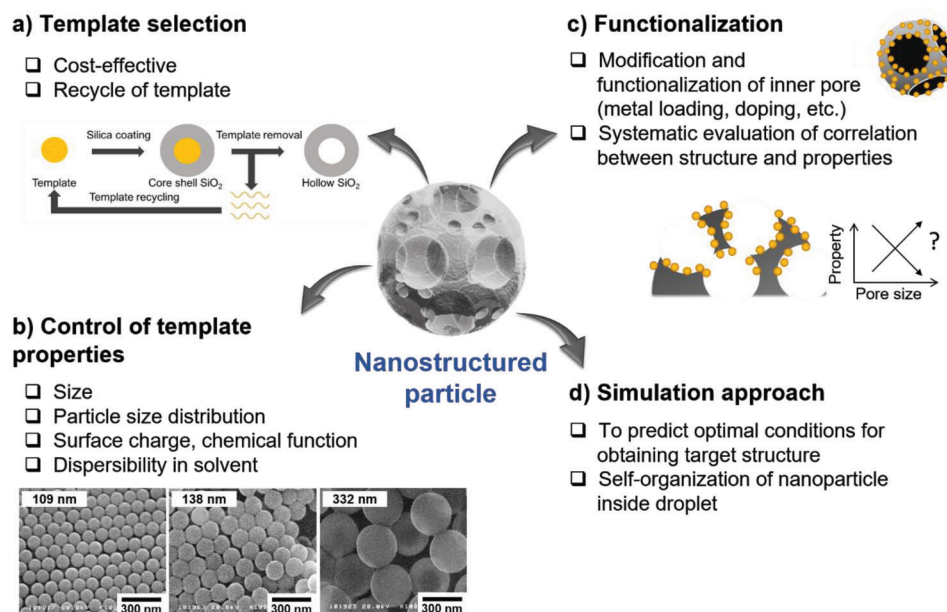
decontamination, among many others.<sup>[38]</sup> The spray-drying synthesis of MOFs (Figure 2b) relies on the formation and further drying of micrometric droplets containing the desired metallic and organic precursors. Rapid evaporation of the solvent induces the formation of nanoscale MOF crystals at the air-liquid interface. These crystals subsequently accumulate and merge into compact or hollow spherical MOF superstructures or beads upon drying.<sup>[37]</sup> Today, a wide range of MOFs (e.g., MIL family, ZIF family, etc.), coordination compounds with functionalities such as thermochromism or spin crossover, and even hydrogen-bonded porous frameworks can be synthesized using spray-drying at the gram- and kilogram-scales.<sup>[39]</sup> A critical aspect in spray-drying synthesis of MOFs is control over reaction kinetics. Indeed, conditions that promote rapid reaction and precipitation upon mixing of the reagents can lead to the formation of amorphous phases or unwanted species before spray-drying even begins. This problem can be resolved through the use of a T-junction connector or a three-fluid nozzle,<sup>[40]</sup> attachments that shorten the contact time between the precursor solutions.<sup>[41,42]</sup> Contrarily, spray-drying syntheses of MOFs containing high-nuclearity clusters (e.g., zirconium-oxo-hydroxo clusters) that require longer reaction times may result in low yields and/or afford materials with poor sorption capabilities, due to fast drying-kinetics. This problem can be overcome by adding a continuous-flow reactor at the entrance of the spray-dryer, to induce nucleation before spray-drying.<sup>[43]</sup>

Spray-drying has also been proven utile in covalent chemistry. For example, it has been used to improve the stability or modify the mechanical properties of polymers, by chemical crosslinking of polymer or biopolymer chains using transformations such as Diels-Alder or click chemistry reactions.<sup>[44]</sup> In other, more recent examples, Schiff-base condensations have been employed for spray-drying modifications of MOFs<sup>[45]</sup> or for the synthe-

sis of covalent organic frameworks (COFs), a class of porous crystalline materials analogous to MOFs, which are created via covalent linkage of organic monomers (Figure 2c).<sup>[46]</sup> A possible explanation for the amenability of these condensations to spray-drying synthesis is that water, which is generated as a side-product during the formation of the condensation product, is spontaneously removed upon entry of microdroplets into the hot chamber. This drives the equilibrium in the forward direction, according to Le Chatelier's principle, thus providing high rates of conversion.<sup>[47]</sup>

#### 2.1.4. Templated Materials Design

Template-assisted spray-drying has emerged as the predominant approach for the synthesis of nanostructured materials.<sup>[13,49]</sup> The incorporation of templates provides insightful guidance for the assembly of new types of nanostructured materials with novel frameworks and compositions, leading to their extended functions and prospects. However, there are still challenges to be addressed for the practical applications of nanostructured particles using the template-assisted spray-drying method. **Figure 3** illustrates important issues that need to be considered in the future to overcome these challenges and further advance the field. Firstly, the selection of an appropriate template is an essential factor in the synthesis of nanostructured materials. One of the key considerations in template selection is its cost-effectiveness and the ability to recycle for multiple synthesis cycles, which may be feasible for large-scale production, and reduce the overall cost as well as environmental impact of the process. The typical templates including  $\text{SiO}_2$ ,<sup>[50]</sup>  $\text{CaCO}_3$ ,<sup>[51]</sup> polymer (e.g., PMMA, PSL),<sup>[52,53]</sup> amphiphilic triblock copolymer (e.g., F127, P123),<sup>[54]</sup> and alkali salt (e.g., NaCl, KCl)<sup>[55]</sup> have been used for the



**Figure 3.** Challenges and perspective for the practical applications of nanostructured particles using template-assisted spray-drying method.

fabrication of nanostructured materials. However, the removal of these organic/inorganic templates may require harsh chemical treatments (e.g., organic solvent, strong acid, or base) or prolonged exposure to high temperatures, which may destroy the structure of the material. Secondly, controlling the properties of used templates plays a significant role in determining the structure, composition, and morphology of the final materials. For example, the use of surfactants can help controlling the size of the template, while surface modification techniques can be employed to tailor the surface charge and chemical functionality of the template. In addition, the selection of an appropriate solvent system can help ensuring the dispersity of the template and promoting efficient assembly of the nanostructured material. The positioning of the template particles within the microsphere is influenced by several critical factors, including: (i) the mixing ratio between the nanoparticles, serving as building blocks, and the template particles, (ii) the size ratio between these nanoparticles and template particles, and (iii) the surface potential of both, the nanoparticles, and template particles. Furthermore, the positioning of template particles is affected by the difference between the solvent evaporation rate of the droplet and the diffusion rate of colloids inside the droplet.<sup>[56]</sup> These factors collectively determine how templates are distributed within the microspheres, impacting the final structure and properties of the resulting nanostructured materials. Thirdly, after removing templates, the inner pore networks of generated products can be further functionalized (e.g., metal loading, heteroatom-doping), which significantly enhances the application scope of the resulting materials. In addition, the systematic evaluation of the correlation between structures and properties is crucial for understanding the underlying mechanisms of the synthesis process and optimizing the performance of the materials. Finally, using a simulation approach is an effective and promising tool for predicting optimal conditions for obtaining the desired target structure in the template-assisted spray-drying method.

#### 2.1.5. Combinations of (a)–(d) (Sections 2.1.1–2.1.4)

Besides pursuing one of the aforementioned four different material formation strategies via spray-drying, a combination of two or more of them is also possible and opens up the design of even more diverse and complex hybrid materials. One approach in this context is the combination of chemical reactions and templating during spray-drying. In a typical process, molecular metallic precursors and templates co-assemble by evaporation-induced self-assembly mechanism to form organic/inorganic nanocomposites. The molecular precursor typically leads to an inorganic continuous network as discussed above (Section 2.1.3). Instead, the organic agents form micelles or other structures, which act as a sacrificial mold for the final porous material (Section 2.1.4). One timely development in the field consists in going beyond porous oxides and ceramics. Starting from molecular precursors, spray-drying synthesis can be extended to fabricate porous metallic materials, including noble metals, with important implications for catalysis for instance. This can be done by using bifunctional polymeric templates, in which polymeric colloids can be used as structuring agents and reducing agents to form a metallic porous network starting from metallic salts by carbothermal reductions at a mild temperature (see Figure 2d, Section 2.1.3).<sup>[48]</sup> Another combined spray-drying approach is the MOF or COF synthesis (Section 2.1.3) merged with the sole assembly of molecular or nanoparticle building blocks (Section 2.1.1). Such composites offer many advantages over other material classes: for instance, they can prevent guest materials from aggregating or degrading in harsh environments; control and sustain the release of guest molecules; and provide superior adsorption or selectivity relative to analogous non-composite materials.<sup>[57]</sup> In this context, MOF-based and COF-based composites incorporating various materials, including inorganic nanoparticles (e.g., Pd, Pt, Au, CeO<sub>2</sub>, and hybrid core-shell Au/CeO<sub>2</sub> nanoparticles), polymers (e.g., polystyrene), organic molecules (such as dyes) and salts, have

been synthesized.<sup>[41,58,59]</sup> In another approach, precipitation reactions during spray-drying (Section 2.1.2) can be combined with different procedures. For example, one way of coupling precipitation and chemical synthesis is co-spray-drying calcium hydroxide and ammonium fluoride precursors to initiate a co-precipitation reaction that yields nanoscaled  $\text{CaF}_2$  powder.<sup>[60]</sup> When composite precursor solutions, consisting of various 3,5-dinitrobenzoates (Fe, Co(Cu)), are united by ultrasonic spray-drying, nanoparticles precipitate in the process and self-assemble into core-shell microstructures, depending on their respective size, therefore successfully enabling the combination of precipitation and nanoparticle assembly (chapter a).<sup>[61]</sup> Further, templated reactions can be linked with precipitation. An example is the preparation of porous SBA-15-type  $\text{SiO}_2$  microparticles (Section 2.1.4).<sup>[16]</sup> Here, TEOS as a precursor for  $\text{SiO}_2$  is spray-dried with polymeric templates (F127 and Eudragit RS). While the former precipitates during spray-drying, the latter is removed in a subsequent calcination step to form porous structures.

### 2.1.6. Processing of Fragile Moieties

Spray-drying processing is primed to solve some of the challenges we face when handling fragile moieties that are needed in hybrid materials, mostly owing to the very short processing time. A first example is the preparation of functionalized oxides, such as hybrid silica or metallo-silicates bearing organic moieties. It is well-known that organosilanes do not react at the same rate as the usual alkoxide precursors (e.g., tetraethyl orthosilicate (TEOS) in silica-based sol-gel chemistry),<sup>[62]</sup> which complicates the one-step preparation of hybrid materials, often leading to inhomogeneous materials. Even when successful, for example using reactivity modifiers, the texture of the material can be strongly affected by the introduction of organosilanes in the synthesis medium. The rapidity of the spray process allows a facile addition of organosilanes to incorporate the needed organic functionality at the surface of the silica. This has been exploited to moderate the hydrophilicity of the materials, as exploited in heterogeneous catalysis.<sup>[63]</sup> Interestingly, in this case, the texture can still be controlled by exploiting templating strategies; this allows exploiting the presence of the organic functionalities without compromising the advantageous textural properties of the mesoporous materials that are accessible via spray.<sup>[64]</sup>

Biological materials can also be processed by spray. In the food industry, the common example is the milk that is dried by spray-drying to give the powder we use to prepare baby formula. Now, when it comes to functional materials, the idea is to maintain the biological activity of the biological moieties that are forced to come together with other components. In one example, spray-drying was used to fabricate highly concentrated, self-assembled type I collagen microparticles enabling the encapsulation of therapeutic biomolecules by preserving the native properties of fragile collagen after drying.<sup>[65]</sup> Spray-drying is thus ideally suited for fabricating ready-to-use collagen microparticles easily injectable for tissue regeneration and 3D bioprinted scaffolds.

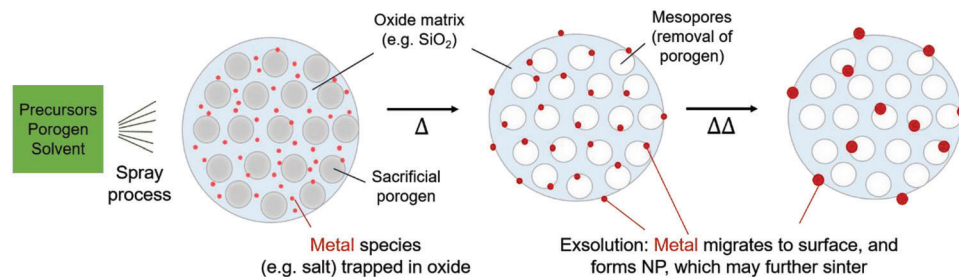
For example, enhancing the storage and thermal stability of active enzymes is of utmost importance, and microencapsulation with appropriate support (e.g., alginate)<sup>[66]</sup> using spray-drying has been demonstrated. In this case, enzymatic activity

was slightly lowered after spray, but an enormous gain in stability was achieved. Hybrid catalysis, as an emerging field where chemo and enzymatic catalysts are teaming up,<sup>[67]</sup> entails the preparation of chemo-enzymatic hybrid materials in which the activity of both partners must be preserved. In the case of very fragile enzymes, these must be stabilized (e.g., via complexation in a polyelectrolyte) forming so-called enzyme-polyelectrolyte complexes,<sup>[68]</sup> to preserve their activity upon processing via spray-drying.<sup>[69]</sup>

### 2.1.7. Formation of “Precursor Materials”

The particles obtained via spray-drying can be exploited as precursors to being further converted into well-defined objects which are otherwise difficult to obtain. For example, tailored zeolite nanocrystals have been formed upon hydrothermal treatment of amorphous metallo-silicate microspheres formed by reactive spray-drying.<sup>[70]</sup> The method takes advantage of the spray process to shape the precursor materials in the form of spherical particles which feature a high concentration and a high dispersion of the heteroatom (e.g., Ti when the TS-1 zeolite is targeted). The porosity is then filled with a structure-directing agent solution and the paste is treated in hydrothermal conditions. As opposed to conventional hydrothermal methods, very low amounts of structure-directing agents and solvent (water) are needed, and the crystallization can be completed at lower autoclave temperatures. In another example, the potential of spray-drying was demonstrated as an alternative synthesis process for the production of perovskite absorbers in powder form. Various Pb-containing and Pb-free perovskites were produced, owing to phase stability and high shelf-life. Subsequently, whenever desired, the produced absorber powders could be used as an “instant powder” starting material for a coating solution and the deposition of absorber layers in solar cell manufacturing.<sup>[71]</sup>

Another approach is the exploitation of spray-drying for dispersing small metal nanoparticles on the surface of a relatively “innocent” support (e.g., silica). Such deposition is often a challenge, due to the poor interactions between the support and the metal, and due to the tendency of the latter to sinter. Taking a sidestep, aerosol-assisted sol-gel allows trapping the metal precursor (e.g., Pd,<sup>[72]</sup> Au,<sup>[73]</sup> Ag,<sup>[74]</sup> Cu salts<sup>[75]</sup>) into the matrix of a (porous) silica material. Even if the metal shows low solubility in silica, its homogeneous dispersion is forced by the rapid polycondensation reactions occurring during aerosol processing. Then, thermal treatment can be used to trigger the migration of the metal toward the surface. This phenomenon is referred to as “exsolution” (in particular when starting from crystalline lattices and applying reducing thermal treatments,<sup>[76]</sup> but also by extension for all cases where a highly dispersed element is forced towards the surface under thermal effect, see **Figure 4**). Playing with the severity of the heating step it is possible to fine-tune the extent of the migration towards the surface and the subsequent sintering to obtain supported nanoparticles of different sizes. Interestingly, the formed nanoparticles—which arise from the bulk of the material—tend to exhibit stronger interactions with their supporting material, and therefore higher stability. Recently, this was successfully exploited to design Cu- $\text{SiO}_2$  catalysts<sup>[77]</sup> and also with other carriers, such as ceria, alumina,



**Figure 4.** Schematic representation of the preparation of metal-based heterogeneous catalysts by the “spray + exsolution” process. A precursor solution containing solvent(s), precursor(s) of the oxidic support (e.g., alkoxides), a sacrificial poregen, and a metal precursor (e.g., chloroauric acid, copper nitrate, palladium chloride, etc.) is aerosolized and dried. In the recovered dried particles, the metal precursor is trapped and homogeneously dispersed into the oxide matrix. Upon thermal treatment, the metal species—which feature low solubility in the oxide—are forced to migrate towards the surface of the particles or pores, where they form small metal or metal oxide nanoparticles. Depending on the severity and duration of the thermal treatment, these nanoparticles can further sinter to form larger nanoparticles. This process may result in materials that are very different (in terms of NP size, size distribution, shape, degree of interaction with the support, spatial distribution, etc.) from those obtained by the more classical deposition (impregnation, deposition, grafting) of metal precursors onto a preformed support. This emerging strategy was shown and is expected to lead to new metal-based catalysts with properties and performance that cannot be reached otherwise.

titania, zirconia.<sup>[78,79]</sup> An important note is that some metal precursors may react very quickly during the spray processing, under the effect of the sudden temperature and concentration increase. They consequently need to be stabilized, e.g., with functional alkoxides. In the case of chloroauric acid that readily decomposes during aerosol processing and forms relatively large nanoparticles embedded inside the support matrix instead of being homogeneously dispersed, the substitution of a small fraction of TEOS by (3-mercaptopropyl)trimethoxysilane (MPTMS) successfully stabilized the gold precursor and led to small ( $\approx 3$  nm) Au nanoparticles after calcination.<sup>[73]</sup>

#### 2.1.8. Post-Treatment of Spray-Dried Material

Based on the extensive experience gained in the formation of a wide variety of materials and structures by spray-drying and on the way to their application, the further processing of spray-dried materials has currently started to attract attention and will continue to do so in the future. The probably most straight-forward post-synthetic treatment of spray-dried materials is their chemical surface functionalization through either covalent coupling reactions (e.g., click chemistry or DDC/EDC couplings) with target molecules such as enzymes, chromophores, or peptides, via reactions with organosilanes (e.g., aminopropyltriethoxysilane),<sup>[80]</sup> or via electrostatic interactions (e.g., carboxylic or phosphonic acids on metal oxide surfaces) with ligands such as surfactants.<sup>[81]</sup> In this context, the post-synthetic loading of spray-dried particles with molecules including drugs, enzymes, dyes, fertilizers, or pesticides with or without attachment onto them should also be mentioned as it enables their application as storage materials.<sup>[82,83]</sup> Furthermore, advanced physical and chemical surface layer deposition methods could also be exploited for post-synthetic surface modifications. Using atomic layer deposition, porous spray-dried iron oxide particles,<sup>[84]</sup> as well as amorphous drug-loaded particles,<sup>[85]</sup> have recently been successfully surface-modified with various metal oxide ( $\text{Al}_2\text{O}_3$ ,  $\text{ZnO}$ , and  $\text{TiO}_2$ ) coatings. In general, post-synthetic surface functionalization may circumvent spray-drying-inherent mate-

rial limitations (see 2.2.) when using fragile substances or permit surface modification that would negatively interfere with the material formation during spray-drying.

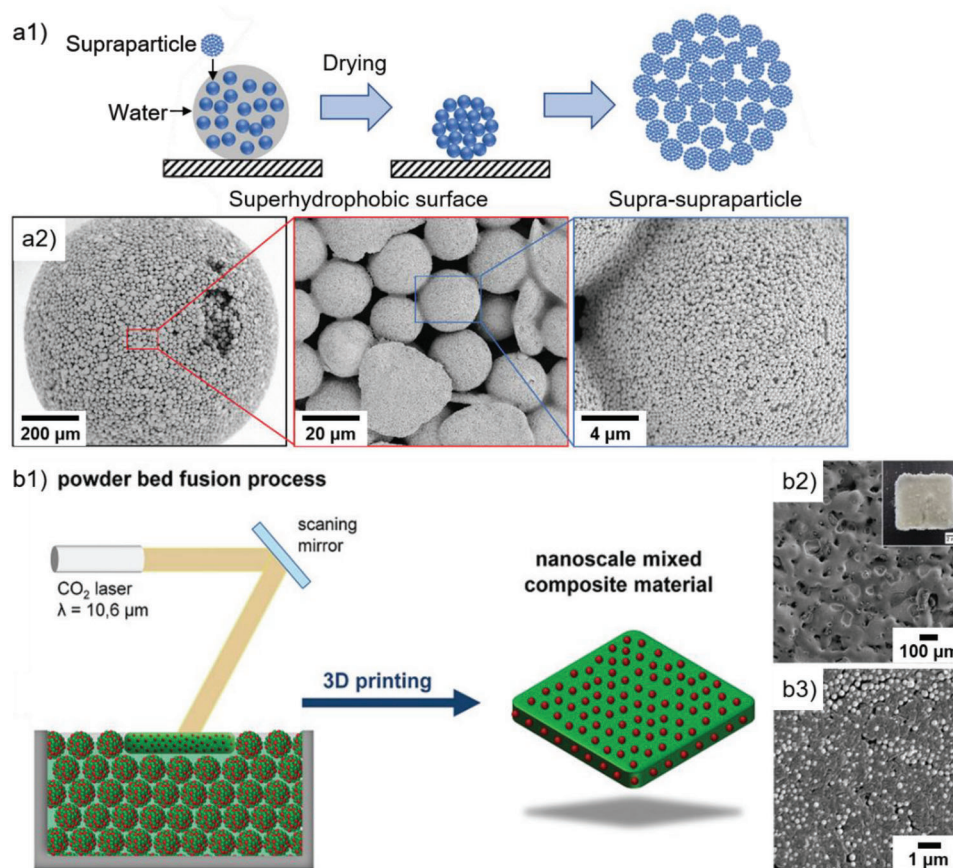
More advanced processing approaches are the creation of a next level of hierarchy based on spray-dried materials as building blocks. In this context, one could imagine the fabrication of particle-based materials of all “dimensions.” For example, “0-dimensional” multi-hierarchical millimeter-scaled particles<sup>[17,86]</sup> have recently been presented. As “2-dimensional” objects first coatings based on spray-dried particles have already been developed<sup>[87–89]</sup> and “3-dimensional” objects can be envisaged via powder-based additive manufacturing<sup>[90]</sup> or could in future be exploited via 3D printing techniques (see Figure 5). The creation of “1-dimensional” objects could eventually also be achieved by transferring nanoparticle assembly concepts<sup>[91]</sup> to the microscale, such as a linear particle arrangement with the help of external fields.

## 2.2. Spray-Drying: Technical Advantages and Limitations

Spray-drying comes with many advantages—but there are also limitations. Both sides of the medal are outlined in the following. Furthermore, this Perspective will focus on material-related formulation opportunities and challenges that are independent of equipment size. Scale transition of spray-drying, for constant formulation properties, will introduce additional operational challenges on the engineering side, e.g., flow field design, avoidance of excessive droplet–droplet or droplet–particle collisions, that merit an own perspective.

On the plus side, as obvious from the previous section, stands out the possibility to enable the design of diverse materials, hybrids, and exotic combinations. A few examples are macro and mesoporous high-entropy-alloy (HEA) particles (Figure 6a),<sup>[53]</sup> silica-enzyme particles (Figure 6b),<sup>[81]</sup> silicon–carbon–graphene combinations (Figure 6c),<sup>[79]</sup> iron oxide–polymer (e.g., polylactic acid) composites (Figure 6d),<sup>[6]</sup> lipid–silica structures containing living cells (Figure 6e),<sup>[80]</sup> zeolite–enzyme–polyelectrolyte





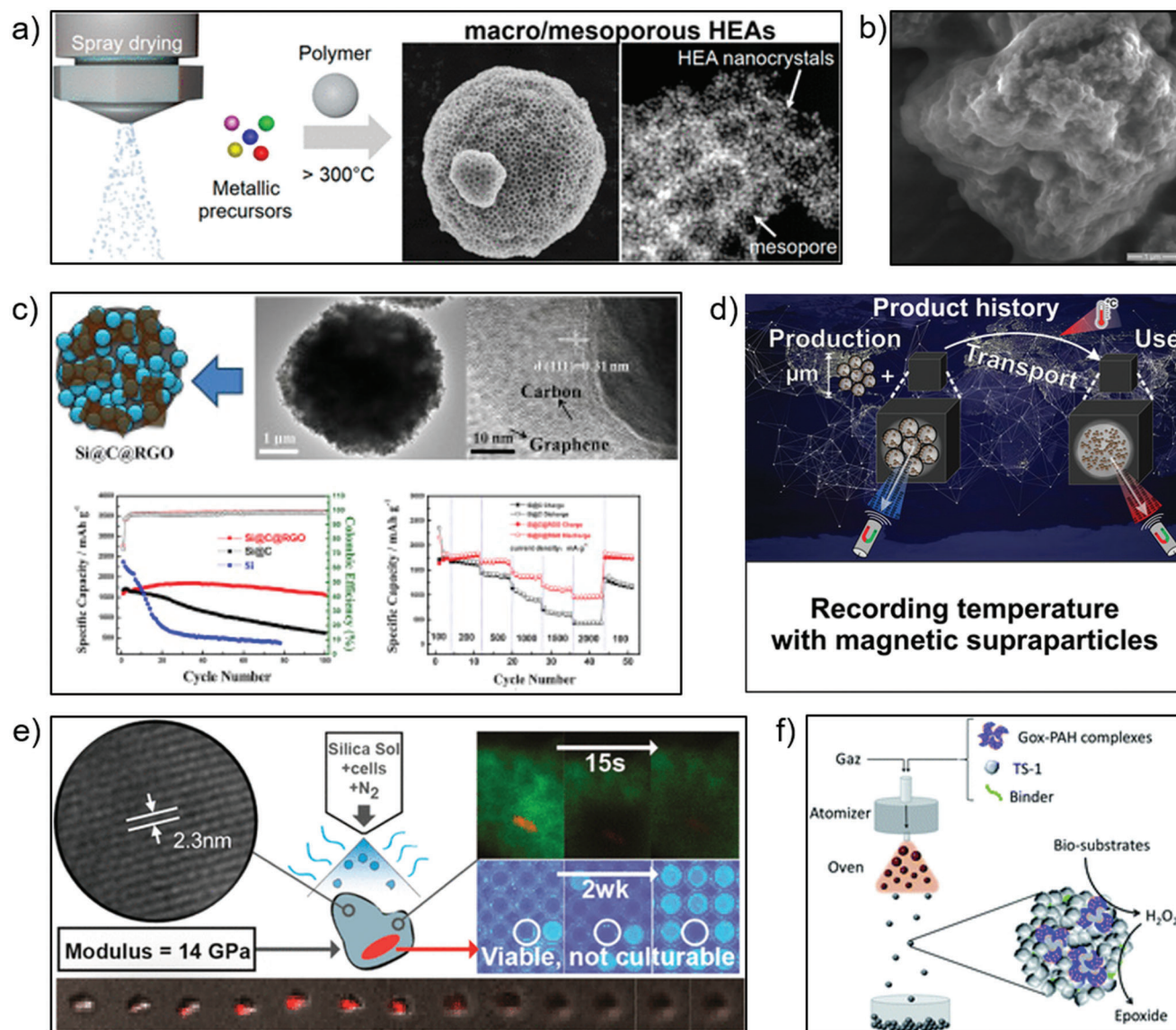
**Figure 5.** a) Particles consisting of supraparticles, b) i.e., supra-supraparticles, and powder-based additive manufacturing using supraparticles. a1,b1) Their fabrication processes are visualized in schemes and a2,b2,b3) SEM studies show the obtained material. b1,b2) Adapted with permission.<sup>[90]</sup> Copyright 2020, John Wiley and Sons. a1,a2) Adapted with permission.<sup>[17]</sup> Copyright 2023, John Wiley and Sons.

hybrids (Figure 6f),<sup>[60]</sup> LiMnO<sub>2</sub>–carbon black materials,<sup>[82]</sup> or iron oxide–MOF hybrids.<sup>[37]</sup>

Moreover, spray-drying is in essence a process based on fast evaporation. Controlling kinetics is of paramount importance in the final chemical composition and the structuration process. From a chemical point of view, the fast drying induces quenching of the system into metastable states. As a result, whatever non-volatile species are in the initial solution, they will be found in the final material with a degree of dispersion that will depend on the chemical affinities and the kinetics of the evaporation-related process. Playing on kinetics has two main advantages. The first important advantage is related to the fact that fast drying promotes the kinetic control of the structuration into local minima through thermal quenching ideally suited to prepare materials with intimate mixing of non-soluble precursors to obtain mixed oxides, alloys, or composites. One representative example concerns the fabrication of high entropy alloys, multi-principal element alloys, composed of five or more homogeneously mixed metals in nearly equimolar ratios.<sup>[53,95]</sup> The second advantage of fast kinetics concerns the structuration and the possibility to achieve controlled matter phase separation. Indeed the evaporation of the droplets taking place at the liquid/air interface leads to thermal and chemical gradients (solutes concentrations, surface tension, and polarity) from this interface towards the heart of the volume.<sup>[96]</sup>

Tuning the drying of the solvent can thus be used as a tool to induce a gradient of properties from the surface to the core to core–shell, graded, or hollow particles of complex structures.<sup>[97]</sup> For instance, spray-drying was used to fabricate porous spheres with a core–shell structure by using a mixed surfactant approach where the shell and the core exhibit different ordered mesoporosity and pore sizes.<sup>[98]</sup> Gradients of precursors concentration can be used to induce controlled phase separation of several compounds (such as salt crystals, nanoparticles, or biomolecules) at the core of spheres.<sup>[99]</sup> Conversely, evaporation-driven gradients of polarity can promote the migration of hydrophobic entities (nanoparticles) at the outer surface of the spheres.<sup>[100]</sup>

Furthermore, spray-drying is unrivaled in its tunability for continuously transforming a solid-containing liquid into a powder consisting of structured particles. The main handles for tuning are gas-side properties (e.g., type of gas, temperature, initial moisture loading, flow configuration (with or against spray direction), flow pattern (laminar, turbulent)), feed properties (temperature (heated, superheated, subcooled), solids concentration, use of surfactants or other chemical enhancers), spray properties (e.g., initial droplet size distribution and velocity distribution, droplet cone (hollow or full), or droplet and particle re-circulation in the apparatus (e.g., by internal classification of particles and refeeding of too small particles; forced agglomeration of droplets



**Figure 6.** Exotic combinations of diverse materials via spray drying. a) Porous high-entropy-alloy particles; b) silica-enzyme (hexose oxidase) particles; c) silicon-carbon-graphene combinations; d) iron oxide-polymer composites; e) lipid-silica structures containing living cells; and f) zeolite-enzyme-polyelectrolyte hybrids. a) Adapted with permission.<sup>[53]</sup> Copyright 2022, American Chemical Society. b) Adapted with permission.<sup>[92]</sup> Copyright 2010, Royal Society of Chemistry. c) Adapted with permission.<sup>[93]</sup> Copyright 2017, Elsevier. d) Reproduced under the terms of the Creative Commons CC-BY license.<sup>[5]</sup> Copyright 2022, The Authors. Published by Wiley-VCH. e) Reproduced under the terms of the Creative Commons CC-BY license.<sup>[94]</sup> Copyright 2015, The Authors. Published by American Chemical Society. f) Reproduced with permission.<sup>[69]</sup> Copyright 2021, Royal Society of Chemistry.

by intersecting spray (also for initiation of reaction-induced precipitation)). Each of these opportunities can be detailed and optimized for a given product; it is up to the expertise and experience of the spray-dryer operator to achieve the best possible product with the least amount of investment (material, energy).

With more and more operational and product characterization data available nowadays, e.g., by extended process monitoring and offline characterization (e.g., electron microscopy, X-ray tomography), spray-drying can profit from the consequent use of AI methods like other disciplines, e.g., catalysis research or particle technology at large.<sup>[101]</sup> The main perspective uses of AI methods in spray-drying are:

- *Exploration of search space for optimized product design:* Finding the right set of operation and material parameters for a desired product property is a multidimensional problem. Within the set of admissible solutions (parameter values), some may fulfill additional constraints, e.g., maximized sustainability of the process and product, or minimum production effort, as demonstrated by Przybyl and Kozala (e.g., deep and convolutional neural networks),<sup>[102]</sup> Ming et al. (particle swarm optimization-enhanced artificial neural network),<sup>[103]</sup> or Fiedler et al. (efficient design of experiments using a multi-step machine learning approach).<sup>[104]</sup>



- *Elucidation of fundamental relationships between operational, material parameters and product properties:* Utilizing spray-drying data across different disciplines, e.g., material science, pharmaceuticals, or food and feed, AI methods may find fundamental relationships between the parameters and product properties, independent of the field of application. For this, a general open-access database, collecting and curating available experimental evidence across the applications, needs to be established by the spray-drying community (academia and industry).
- *Data-driven modeling for process monitoring and control:* AI methods must be consequently used to develop fast, robust, and computationally efficient surrogate models for spray-drying. This will then allow large-scale optimization of spray-drying processes (e.g., considering whole process chains) as well as allow for improved process monitoring and control of spray-dryer operation. Monitoring and control will for instance not only enable improved product quality but also reduce off-spec product quantities, and operational failures, thereby contributing to sustainable process operation.

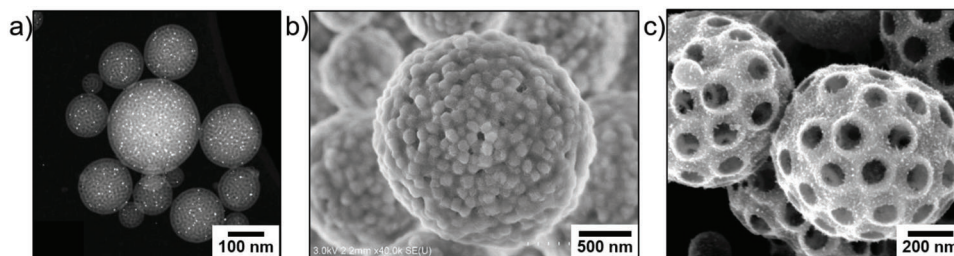
However, in spray-drying, there are also challenges: Spray-drying as a thermal drying process relies on the phase transition of the solvent from liquid to vapor. The phase transition is typically highly energy-intensive, e.g., water has a specific evaporation enthalpy of about 2250 kJ per kg, ammonia of 1369 kJ kg<sup>-1</sup> and ethanol of 846 kJ kg<sup>-1</sup>. Typically, these theoretic minima are not met (with excess in the range of 50 and 150%) which renders spray-drying one of the costliest and by energy demand environmentally very challenging drying processes. Another challenge is the typically low temperature of the exhaust (i.e., moist) gas which is hard to integrate into other process units. To achieve a more sustainable and environmentally friendlier process, typically: 1) high gas (outlet) temperatures or 2) high solids contents in the initial droplets are sought. In case (1), the low moisture loading and high temperature allows for easier integration in other process steps, but results in low efficiency in the use of the drying capacity of the gas; in case (2), earlier crust formation may set in, leading to either hollow particles or fractured particles, if the remaining liquid is trapped and the generated vapor fractures the formed shell. Huge gains in energy efficiency can be obtained by: 3) switching to different solvents with lower specific evaporation enthalpy (if permissible), 4) consequent recovery of the latent heat from the outlet gas. Especially the last option is very promising, if instead of a carrier gas the superheated vapor is used for spray-drying. In that case, the liquid can be removed easily from the outlet gas by condensation. The use of superheated steam has been considered, e.g., in the food and dairy industry.<sup>[105]</sup> A fundamental understanding of the high temperatures on drying kinetics and achievable particle properties is still lacking. Also, a balance between the competing interests of product quality, process efficiency, and environmental impact, still needs to be found.

Another challenge in spray-drying is that precursor solutions/dispersions can be complex mixtures comprising a myriad of ingredients, including nanoparticles, sol-gel inorganic or hybrid polymers, oligomers, organic molecules, metal salts, and surfactants. The stability of the precursor solution/dispersion before atomization is crucial, as it strongly influences the physical and chemical properties (e.g., particle size, morphology, crys-

tallinity, etc.) of the final product. To obtain a homogeneous solid product, this solution/dispersion must be kinetically stable for the entire duration of the atomization process, which can range from minutes to hours. Indeed, unstable solutions or suspensions can cause various problems. For instance, they can block the spray-dryer nozzle, leading to inconsistent droplet formation and particle-size distribution; and they can provoke the formation of unwanted byproducts such as agglomerates, non-homogeneous samples, and unstable particles, ultimately affording the final product in low yields. Additionally, the synthesis of some materials is time-dependent, and the evolution of the reaction or the aging time during the processing of the precursor solution can dramatically affect subsequent atomization.<sup>[30]</sup> Such is the case for many sol-gel-derived syntheses of metal-oxo polymers, as both the size and degree of condensation are time-dependent, and the aging time can drastically influence the texture of the resulting spray-dried polymeric products. Similar problems have been observed in the spray-drying synthesis of high-nuclearity beads of MOFs. To avoid clogging of the nozzle or low crystallization of the MOF beads, the activation time of this process should be precisely controlled before atomization. This is achieved through a continuous-flow reactor, where the primary nucleus of the MOF is grown.<sup>[43]</sup> Accordingly, researchers have dedicated great effort to optimizing the stability of the feed solution/dispersion. Strategies include optimizing the formulation of the suspension, adding appropriate stabilizers, or, in some cases, keeping the dispersion in the feed vessel under constant agitation to facilitate the mixing of ingredients and prevent any sedimentation or separation, or even continuously preparing the suspension just before atomization.<sup>[97,106]</sup>

Mechanical stability is very often a desired property, either for intermediate processing or as a final product quality indicator in specific applications such as dental restoration. In the latter, stable spray-dried nanoparticle clusters made up of multiple nanofillers are employed in high-performance dental resin composites.<sup>[107]</sup> Mechanical stability can in principle be achieved in various ways, for example, by designed slurry properties (e.g., size and shape distribution of primary particles, surface charge distribution, tailoring particle-particle interaction<sup>[108]</sup> and particle microstructure<sup>[109]</sup>), by the use of additives (e.g., clays in porcelain manufacturing<sup>[110]</sup> to improve bonding, plasticity, and deformability), or by chemical reactions during drying that improve bonding of suspended primary particles. In general, while smaller primary particles yield a higher deformation resistance in the structures formed by spray-drying, fracture stress and strain of the resulting supraparticles depend directly on their diameter. If highly mechanically stable primary particles (e.g., silica) are used, the spray-drying process leads to less stable supraparticles as less energy is needed to break the weaker inter-particle bonds than to deform the primary particles.<sup>[111]</sup> Another operational dimension to improve mechanical stability is by selection of drying conditions, i.e., to avoid too fast evaporation rates that either yield hollow particles with thin solid layer or avoid excessive pressure generation during drying leading to deformed or cracked particles.<sup>[108,112]</sup>

Regarding the processing of fragile materials, e.g., enzymes, via spray-drying, the shear stress acting on the droplet, the process temperature (despite its variability over a wide range) as well as sudden liquid-to-solid interface changes during this process



**Figure 7.** Example of tailored heterogeneous catalysts: a) mesoporous Au-SiO<sub>2</sub> catalyst featuring small (3–4 nm) gold nanoparticles, b) hollow zeolite microspheres in which enzymes can be loaded and trapped to form a chemo-enzymatic catalyst, c) macroporous IrO<sub>2</sub> electrocatalysts for proton exchange membrane water electrolyzers. a) Adapted with permission.<sup>[73]</sup> Copyright 2022, American Chemical Society. Reproduced with permission.<sup>[83]</sup> Copyright 2019, Royal Society of Chemistry. c) Adapted with permission.<sup>[125]</sup> Copyright 2018, John Wiley and Sons.

represent essential challenges. This is why they require new approaches or modifications to classical spray-drying. One option, particularly suited for temperature-sensitive products, is spray-freeze-drying. There, the spray is propelled in a very cold environment, e.g., liquid nitrogen, producing solid particles. The solvent is then removed by sublimation. First applications have been presented in the field of biotics,<sup>[113]</sup> while the requirements and opportunities for the generation of nanostructured particles have not been explored for this technique.

### 2.3. Applications of Spray-Dried Structures

In the following, we outline the fields of applications where we foresee the greatest potential and dynamic development for spray-dried materials. We do not attempt to review the current state of the art (which for some of the discussed application fields has been reviewed recently<sup>[12]</sup>) but rather aim at giving exemplary insights and draw a vision of what could become possible in the fields of: I) catalysis, II) diagnostics, III) purification, IV) storage and V) information.

#### 2.3.1. Catalysis

Heterogeneous catalysis is at the heart of a large majority of chemical processes, and our ability to engineer these functional materials at the nanoscale is considered as key for a transition towards more sustainable horizons in industrial chemistry.<sup>[114]</sup> Advanced photo-, electro-, and thermal catalysts are exploited in crucial processes such as hydrogen production, CO<sub>2</sub> reduction, and pollutant degradation. Considering the objective to shift from a petro-based society toward a bio-based one, it has become evident that a new generation of catalysts is needed.<sup>[115]</sup> While petrochemicals are rather apolar and must mainly undergo functionalization reactions, bio-based chemicals are generally polar and must undergo de-functionalization before entering subsequent chemical processes and products.

Spray-drying techniques come in handy to tackle some of the existing challenges in heterogeneous catalyst preparation. Heterogeneous catalysis is a phenomenon that takes place at the surface of a solid that exposes catalytically active sites. Hence, in most cases, the idea in catalyst preparation is to disperse an active component onto a porous carrier, to maximize the active

surface and the utilization of the (often expensive) active element. This is classically obtained by impregnation or grafting methods. A forthcoming approach is to use reactive aerosol processing to trap and disperse active metal species in the matrix of another (porous) oxide. From that point on, depending on the type of catalyst that is targeted, two phenomena can be exploited: mobility or miscibility. First, (noble) metals may have a low miscibility in the surrounding oxide, and a simple calcination leads to their “exsolution” from the bulk of the materials towards its surface (see Figure 4).<sup>[72,79]</sup> Once on the surface, further migration and sintering can occur, depending on the severity and duration of the thermal treatment. The protocols can be finely tuned to promote mobility and adjust metal nanoparticle size (Figure 7a). Interestingly, the fact that the metal nanoparticles emerge from the bulk of the carrier—instead of being deposited on top of it—was found to enhance the stability of metal nanoparticles during catalytic reactions, for example in the dehydrogenation of ethanol to acetaldehyde.<sup>[77]</sup> This “metal exsolution” strategy will probably offer new opportunities for the preparation of metal-based catalysts, and possibly bimetallic or multimetallic catalysts. Indeed, synergy between various metals is a common phenomenon in heterogeneous catalysis, when gains are obtained in terms of intrinsic activity, selectivity, or stability when blending two (or more) metals.<sup>[116]</sup> Classical two-step methods which involve the impregnation or deposition of the metals on the surface of a preformed support offer limited control over nanoparticle formation, (de)alloying, and metal-support interactions. Here, starting from a situation where all metal species are first dispersed in the support matrix, and then forced to migrate towards the surface to form supported particles will expectedly provide new opportunities to tune these formulations. Second, it is possible to leverage rapid aerosol-assisted sol-gel polycondensation reactions to stabilize homogeneously dispersed metal oxide species. In fact, many active sites in heterogeneous catalysts consist of highly dispersed (isolated) metal oxide species, while more condensed species (oligomeric, polymeric, or crystalline oxide species) may be catalytically inactive. Aerosol-assisted solgel methods have been shown to allow stabilizing formulations that feature a high degree of dispersion. The high proportion of isolated metal oxide species (e.g., Ti sites in selective epoxidation,<sup>[117]</sup> Mo sites in olefin metathesis,<sup>[118]</sup> Ga sites in acetalization,<sup>[119]</sup> etc.) allowed reaching high activity. An impending approach exploits simultaneously both strategies to prepare bifunctional catalysts. Recently, a mesoporous Au-Sn-SiO<sub>2</sub>



catalyst was prepared in one step by an aerosol-assisted sol-gel synthesis.<sup>[120]</sup> Upon calcination, isolated Sn oxide species were stabilized in the silica matrix, and small gold nanoparticles were formed at its surface. The catalyst was able to catalyze the oxidation of glycerol (on Au NP) and the rearrangement of the formed dihydroxyacetone with methanol (on Sn species), to yield the targeted methyl lactate. Importantly, the spatial proximity between the two catalytic active species of this bifunctional catalyst favored a faster substrate channeling, thereby hampering the formation of side products and favoring high yield for the final product. It should be noted that previous attempts to prepare such bifunctional catalysts using classical preparation methods were unsuccessful.<sup>[121]</sup>

Hybrid materials are also important in heterogeneous catalysis. Tuning the hydrophilicity of the catalyst surface can serve to boost catalytic performance, by controlling the adsorption behavior of reactants, intermediates, products, or poisons.<sup>[122]</sup> Using functionalized (methylated or fluorinated) alkoxides, one-pot aerosol-assisted sol-gel was shown to provide easy access to various surface-functionalized oxide formulations; this was exploited to enhance hydrophobicity and thereby boost reaction rates in organic reactions that generate water as one of the products.<sup>[63]</sup> In a similar way, the method is expected to provide a platform for the synthesis of catalysts with tailored molecular active sites. For example, thiol function can be oxidized to sulfonate, and exploited in acid-catalyzed reactions. Aminated functions can be used to “click” molecular catalysts.

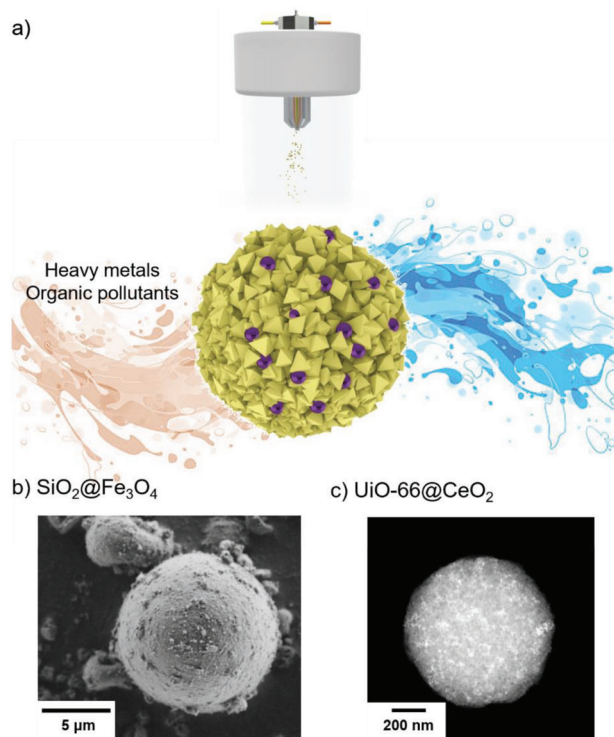
Finally, the tremendous opportunities offered by enzymes should not be overlooked when it comes to the development of more sustainable chemical processes. Yet, many useful catalytic functions are missing in the biocatalytic toolbox, and, to harness the power of enzymes, it is essential to envisage their immobilization,<sup>[123]</sup> and their use in conjunction with chemocatalysts and in particular with heterogeneous catalysts.<sup>[67]</sup> In this particular field of “hybrid catalysis”, advanced particle design is essential to bring together components that are essentially very different. Processing enzymes directly in spray-drying is challenging because these fragile proteins are prone to rapid deactivation. Thus, stabilization strategies have to be developed. In this perspective, it was shown that enzymes can be protected when complexed with polyelectrolytes (e.g., poly(allylamine hydrochloride)<sup>[69]</sup>), or with biopolymers (e.g., chitosan<sup>[66,124]</sup>), and this allows preparing solid hybrid biocatalysts. Other stabilization methods, for example using reverse micelles, or crosslinked enzyme aggregates, could become handy in this perspective. In another approach, spray-drying can be exploited to prepare hollow microstructures, of which the central cavity is exploited to load and trap a controlled amount of enzyme (Figure 7b). The concept was demonstrated for the combination of glucose oxidase and TS-1 zeolite nanocrystals (for which hybridization by adsorption or grafting yielded mediocre results).<sup>[83]</sup> In a “Lego-like” fashion, starting from any kind of nano-objects (e.g., clays, zeolites, nanoparticles) and any kind of enzymes, we foresee that such an approach will allow the preparation of complex hybrid catalysts featuring various chemo- and enzymatic active species, of particular interest in cascade chemical reactions.

Spray-drying also has a great potential to serve the current efforts towards a sustainable energy transition as it offers a ver-

satile and efficient approach to preparing electrocatalysts for applications in fuel cells, electrolysis, batteries, and other electrochemical technologies based on catalytic layers. Ideally, the electrocatalysts must meet several requirements: high electrical conductivity (percolation of the electron conducting network), high electrocatalytic activity, high porosity, and accessibility for liquid and gas transport. The ideal catalytic material must be fabricated via green, and cost-effective processes, compatible with current industrial deposition methods, based on catalytic inks.<sup>[126]</sup> Spray-drying enables the fabrication of particles with control over the size, morphology, porosity, and high surface area, which can enhance electrocatalytic performance by providing more surface area for electrochemical reactions to occur and by favoring mass transfer. In addition, spray-drying facilitates the homogeneous mixing of the precursor materials, resulting in a high and uniform distribution of active sites on the surface of the electrocatalyst. Most of the current examples of spray-dried electrocatalysts concern carbon-based spheres decorated or doped with metal catalysts for oxygen evolution reactions (OERs),<sup>[127]</sup> methanol electro-oxidation<sup>[128]</sup> or the hydrogen evolution reaction (HER).<sup>[129]</sup> In a highly promising example, bifunctional electrocatalysts composed of doped mesoporous carbon-based microspheres were made by spray-drying from cost-effective and biological precursors from eggs.<sup>[130]</sup> For the challenging OER in proton exchange membrane water electrolyzers, only expensive and rare Ir-based materials combine high activity and stability.<sup>[126]</sup> In this context, recently several spray-dried porous Ir-based catalysts have been fabricated showing outstanding activity and stability, as shown in Figure 6c.<sup>[125,131]</sup> While still in its infancy, spray-drying represents an emergent tool to design such multifunctional electrocatalytic materials. Future perspectives could consist in integrating additional structural features to manage and control bubble formations or additional functions such as self-healing or light or magnetic-responsive materials to boost the electrocatalytic activity.

### 2.3.2. Diagnostics (Ex Vivo)

While we refrain from giving a perspective on in vivo diagnostics (as this lies outside the authors' expertise and is rarely addressed with spray-dried materials<sup>[132]</sup>), ex vivo diagnostics displays a broad application field and includes from our point of view sensing (detection/recording/indication) of chemical substances (gases, solvents, biomolecules, ions, ...) and physical conditions (temperature, humidity, mechanical forces, ...). Diagnostics for these purposes are usually based on a molecular recognition or a physical/chemical change resulting in optical or electrical signal changes of the respective molecule or (nano)material. Spray-drying of such building blocks, e.g., together with a support matrix or templates, offers their size increase for facile handling and the creation of highly porous hybrid materials. Diverse spray-dried materials have already been proven to serve this purpose;<sup>[12]</sup> e.g., as temperature,<sup>[5,27,133]</sup> gas,<sup>[88,89,134]</sup> dopamine<sup>[135]</sup> or mechanical sensors,<sup>[136,137]</sup> to name but a few. As diverse sensing building blocks can be flexibly combined via the spray-drying process, the creation of materials capable of sensing multiple triggers at once is conceivable in the future. These may significantly contribute to the development of highly miniaturized sensor



**Figure 8.** a) Schematic illustration of water purification using spray-drying-derived composite materials, such as b,c) silica@Fe<sub>3</sub>O<sub>4</sub> (b) and UiO-66@CeO<sub>2</sub> (c). b) Adapted with permission.<sup>[138]</sup> Copyright 2018, John Wiley and Sons. c) Adapted with permission.<sup>[58]</sup> Copyright 2020, American Chemical Society.

arrays but will also come along with new research challenges regarding materials cross-sensitivities, spectral cross-talk, or cross-leaching of sensitive agents. Future developments in, e.g., biological sensing molecules will extend the library of available sensitive building blocks—given their sufficient stability for their spray-drying processing—and may boost the application of spray-dried sensor materials in the current but also in new application fields.

### 2.3.3. Purification

Water is a finite and non-substitutable resource, which is essential for our life, industry, and agriculture. This is why the management of water resources and especially, water treatment and purification, are of imminent importance. Water purification is the process of removing undesirable chemicals, biological contaminants, suspended solids, and gases from water. In this process, spray-drying can be valuable as a versatile method to design, produce, shape, and scale up new materials that can efficiently adsorb and remove contaminants from water (Figure 8a). For instance, simply the superior structural properties (e.g., defined porosity) that can be obtained from spray-drying nanoscale building blocks are exploitable for water purification, such as the ultrafast dye removal from wastewater (Figure 8b).<sup>[138]</sup> Also, we envision the use of spray-drying to create superior adsorbent composites by mixing two or more materials able to capture contam-

inants. These composites can exhibit synergic or collective adsorption properties that can target the simultaneous removal of multiple contaminants, or that can improve their removal performance for a specific contaminant. Following this strategy, Liu et al. used spray-drying to produce starch-chitosan hydrogel microspheres that can simultaneously adsorb organic dyes (methylene blue and Eosin Y) and several heavy metal ions (Cd<sup>2+</sup>, Cu<sup>2+</sup>, and Ni<sup>2+</sup>).<sup>[139]</sup> More recently, the excellent adsorption capacities of porous MOFs (in particular, UiO-66 and UiO-66-(SH)<sub>2</sub>) and inorganic nanoparticles (in particular, cerium-oxide NPs) were combined to form spherical, microscale bead-like composites that can efficiently and simultaneously remove multiple heavy metals from water, including As(III and V), Cd(II), Cr(III and VI), Cu(II), Pb(II), and Hg(II) (Figure 8c).<sup>[58,140]</sup>

### 2.3.4. Storage

Supraparticles have unique properties and characteristics that make them ideal for storage applications. In recent years, advanced rechargeable batteries and supercapacitors with high energy/power density and long cycle life are intensively researched to meet the needs of various energy storage systems.<sup>[141]</sup> Despite significant progress in developing new materials in this field (e.g., carbon-based materials, transition metal oxides, alloys, and metal chalcogenides), several challenges should be addressed. One of the main challenges is achieving high electrochemical performance. This requires a deep understanding of the underlying physics and chemistry of the superparticles, as well as the ability to control their size, shape, composition, and surface chemistry. Another challenge is the limited stability of the supraparticles, particularly in the presence of moisture and high temperature. This can result in a decrease in their performance and efficiency over time. There are several solutions that can address the current situation. One of the most promising solutions is the use of advanced materials and surface coatings that can enhance the stability, performance, and durability of the supraparticles. For example, the use of carbon-based materials (e.g., graphene, carbon nanotubes) can improve the electrical conductivity and stability of the supraparticles. Similarly, the use of surface coatings (e.g., polymers, silica, metal oxides) can protect the supraparticles from moisture and high temperature and enhance their surface chemistry for better interaction with the electrolyte.

Supraparticle-based storage can be not only considered in terms of energy but also in substance storage, such as in the field of agriculture pesticides<sup>[142]</sup> and fertilizers<sup>[143]</sup> or in the field of biomedicine drugs.<sup>[144]</sup> In these fields, the stability of supraparticles (as carriers) during storage and handling is important.<sup>[145]</sup> However, supraparticles may agglomerate or degrade over time (on purpose or accidentally), which can affect their properties and performance. On the other hand, the optimization of the drug-carrier ratio and spray-drying conditions to achieve optimal substance loading and release behavior is essential. To address these challenges, for drug delivery applications, the use of natural biopolymers (e.g., chitosan, alginate) can improve the stability and mucoadhesive properties of the supraparticles, which can enhance their efficacy. Another solution is the addition of surfactants or co-solvents to the spray solution, which can enhance the stability of the drug and carrier material, leading to more

efficient drug loading and release. In the case of fertilizer or pesticide delivery systems, the focus also is on natural biopolymers (e.g., chitosan or cellulose) that are available at low cost, do not release any toxic substances to the environment, and are fully degradable after completion of the delivery process. The use of novel carrier materials (e.g., MOFs, mesoporous silica) can provide high surface area and tunable pore size, which can improve the loading and release of active ingredients in the supraparticles.

The significance of encapsulation becomes evident through the application of spray-drying in various fields, particularly in the domain of material science and engineering.<sup>[146]</sup> One area where encapsulation plays a critical role is in the development and design of inorganic–organic healing agents for self-healing concrete, offering transformative perspectives for enhancing the durability and resilience of civil infrastructure.<sup>[147]</sup> The spray-drying enables the creation of micrometer-sized particles that can encapsulate healing agents effectively. This encapsulation shields the healing agents from direct contact with the harsh environment (concrete), ensuring their protection and controlled release when cracks form. By incorporating inorganic–organic healing agents (e.g., minerals and polymers) into the encapsulation process, synergistic benefits can be achieved, where the inorganic components provide mechanical reinforcement, and the organic components offer flexibility and self-healing capability. The versatility of spray-drying allows for precise control over particle size, morphology, and composition, resulting in improved compatibility and durability of the encapsulated agents within the concrete matrix. The perspectives of spray-drying in this domain are promising and forward-looking, as ongoing research explores innovative approaches to optimize the encapsulation process, tailor the release kinetics of healing agents, and enhance the overall performance of self-healing concrete. The utilization of spray-drying for encapsulation not only underscores the significance of encapsulation itself, but also opens new avenues for advancing the field of self-healing materials, particularly in the area of concrete technology. Furthermore, the integration of responsive polymers, smart materials, and sensor networks can elevate the capabilities of self-healing concrete, creating a dynamic infrastructure that adapts and repairs in real-time.

In addition, there are also challenges specific to the spray-drying method that must be considered. One major challenge is controlling the size, shape, and morphology of the supraparticles produced using spray-drying, as well as achieving uniform dispersion of the starting materials and/or templates. To address these challenges, the development of new types of templates or solvents to achieve more precise control over particle properties is highly desirable. By addressing these challenges and perspectives related to the spray-drying method, researchers can continue to improve the synthesis of supraparticles using this approach and enable further advancements in the fields of storage applications.

### 2.3.5. Information carriers and providers

Recently, the concept of communicating supraparticles (CSPs) was introduced.<sup>[148–150]</sup> CSPs are supraparticles that are equipped with nano building blocks that deliver a unique identification (ID) pattern for each particle. Moreover, the supraparticles are equipped with building blocks that are specifically vulnerable to

environmental stimuli. Taken together, such a supraparticle is capable of reporting its identity and its history (in terms of experienced environmental triggers).<sup>[148]</sup> Such particles are envisioned to be easily applicable as additives to employ arbitrary materials with intelligence, i.e., to enable perceptual matter.<sup>[148,151]</sup> This is of great interest as it would deliver the bridge to connect the materials with the modern, digital world (**Figure 9**) and enable tracking and tracing of objects, predictive maintenance, recycling, and many more applications.<sup>[152]</sup>

To create CSPs, nano and also molecular building blocks with characteristic physical properties need to be joined. These building blocks might be very different, for instance, to enable an optical or magnetic ID, nano and molecular moieties such as organic dyes, lanthanides, MOFs, quantum dots, nanosilica, nano-polymer-particles, nano-iron-oxides, and many more are employed.<sup>[6,7,21,137,148]</sup> Often, the ID is based on ratiometric and spectral pattern principles that can be designed via a flexible choice of building block combinations and ratios.<sup>[6,148,153]</sup> This flexibility in choice is key and can only be guaranteed if the process of joining the building blocks comes without too many restrictions, i.e., this is another example where spray-drying is superior compared to many other techniques. Furthermore, in order to incorporate these intelligent particles into materials, the processing of CSPs should be possible in a similar manner to standard additives. The fact that spray-drying produces a micrometer-sized, free-flowing powder further enhances the benefits of using CSPs.

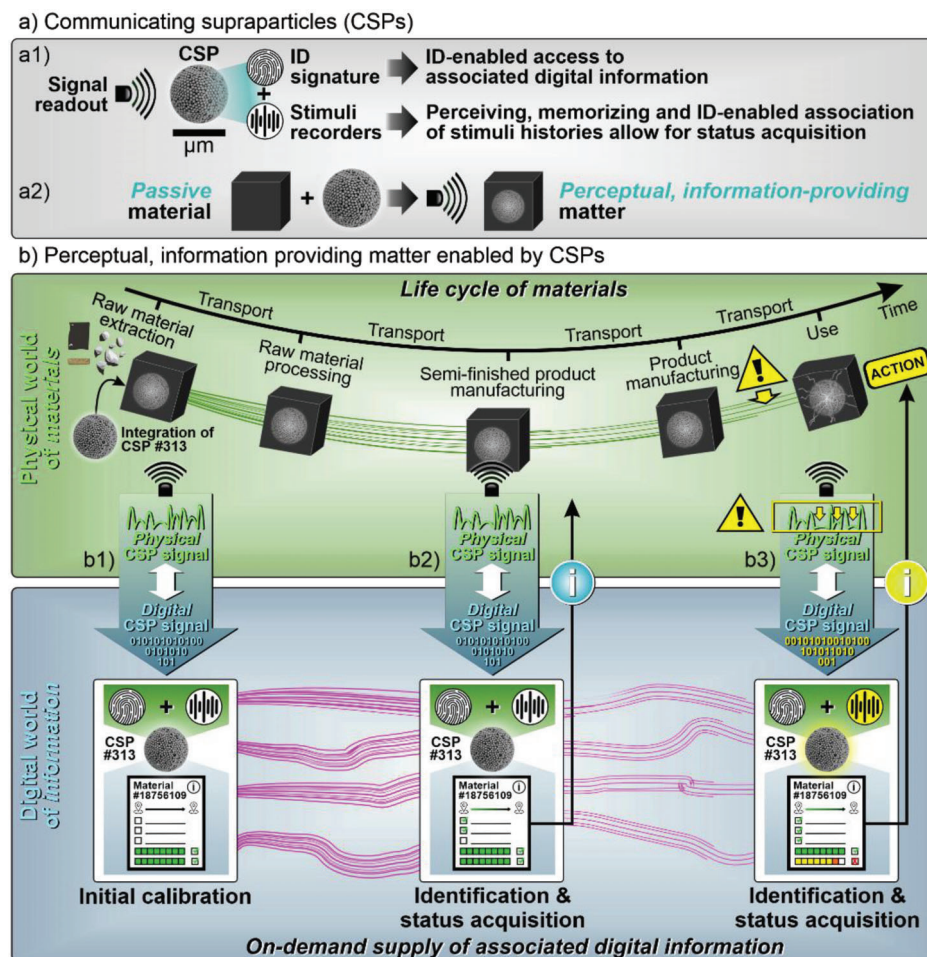
Designing functional CSPs for all application aspects as mentioned above will be a long journey and will require a lot of effort to precisely control building block arrangement, structure, and thereby interaction and ultimately cooperative interplay in the whole supraparticle to yield the desired interactive functionalities. To succeed in this endeavor, the precise arrangement of building blocks upon spray-drying will be crucial and will demand further research—but will be rewarded with a direct application perspective as spray-drying ensures that a scalable way of manufacturing is right at hand.

## 3. Conclusion

In our view, spray-drying is a technique whose potential has been underestimated by most (material) chemists today. The simple tool has undeservedly been neglected as part of a materials chemist's laboratory. Clearly, one has to be open to leaving the possibly more familiar world of wet chemistry and dealing with a transition of wet chemistry to the gas phase to ultimately end up with a solid phase.

Also, one has to accept to leave the regime of thermodynamic control and enter the world of fast kinetics—where control is more difficult to obtain and where deep insights, e.g., regarding formation aspects, are hard to gain. Understanding fully the processes and mechanisms that occur when doing chemistry in a spray-dryer will still be a long journey and will require the close collaboration of chemists with engineers, theoreticians, modeling experts, and physicists. Additionally, it is of utmost importance to further address the challenges of spray-drying such as the continuous development of new technological advances in spray-dryers to cover the synthesis of more molecules and materials using different chemistries. In this way, this could enable





**Figure 9.** The concept of communicating supraparticles (CSP) to bridge the analog and the digital world. Reproduced under the terms of the CC-BY Creative Commons Attribution 4.0 International license (<https://creativecommons.org/licenses/by/4.0/>).<sup>[150]</sup> Copyright 2023, The Authors, published by Wiley-VCH.

the use of spray-drying in fields where it is still underused, for example, organic chemistry. Furthermore, it would become possible to use spray-drying in more “extreme” conditions such as spray-freeze-drying, spray pyrolysis, or even in coupled processes with other stimulations such as radiations, light, magnetic fields, or reactive gases.

But progress in this field is considered as highly rewarding, as spray-drying enables fast, easy, and simple creation of very new multifunctional, hybrid material types and classes, considering that any combinations of nanoparticles or molecules and in situ chemistry (“chemistry in a droplet”) is in principle possible—often independently of the original chemistry or classical chemical reaction-constraints. In particular, we expect many high-performance materials in diverse application fields in the near future that will attract the attention of materials chemists more and more towards spray-drying.

## Acknowledgements

S.W. and K.M. gratefully acknowledge funding by the NanoMatFutur grant 03XP0149. K.M. and A.B. acknowledge funding by the project

CRC1411 (Deutsche Forschungsgemeinschaft (DFG, German Research Foundation)- Project-ID 416229255 - SFB 1411).

Open access funding enabled and organized by Projekt DEAL.

## Conflict of Interest

The authors declare no conflict of interest.

## Keywords

chemistry in a droplet, functional materials, hybrid materials, nanoparticle assembly, spray-drying, structure formation, supraparticles

Received: July 7, 2023

Revised: August 30, 2023

Published online: October 15, 2023

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