Topical Review

Vapor phase processing: a novel approach for fabricating functional hybrid materials

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Abstract

Materials science is nowadays facing challenges in optimizing properties of materials which are needed for numerous technological applications and include, but are not limited to, mechanics, electronics, optics, etc. The key issue is that for emerging applications materials are needed which incorporate certain properties from polymers or biopolymers and metals or ceramics at the same time, thus fabrication of functional hybrid materials becomes inevitable. Routes for the synthesis of functional hybrid materials can be manifold. Among the explored routes vapor phase processing is a rather novel approach which opts for compatibility with many existing industrial processes. This topical review summarizes the most important approaches and achievements in the synthesis of functional hybrid materials through vapor phase routes with the goal to fabricate suitable hybrid materials for future mechanical, electronic, optical or biomedical applications. Most of the approaches rely on atomic layer deposition (ALD) and techniques related to this process, including molecular layer deposition (MLD) and vapor phase infiltration (VPI), or variations of chemical vapor deposition (CVD). The thus fabricated hybrid materials or nanocomposites often show exceptional physical or chemical properties, which result from synergies of the hybridized materials families. Even though the research in this field is still in its infancy, the initial results encourage further development and promise great application potential in a large variety of applications fields such as flexible electronics, energy conversion or storage, functional textile, and many more.

Keywords: hybrid materials, vapor phase processing, ALD, MLD, VPI, SIS, CVD

(Some figures may appear in colour only in the online journal)

1. Introduction

The properties of materials, being building blocks of anything that surrounds us, have always been of crucial importance for the development of our society. Mankind has learned to develop and use tools out of suitable materials in order to shape others and in this way make them useful for anything that needed to be built. Over the centuries the selection of materials passed various phases, from wood and stone, various metals including copper, bronze, iron, towards polymers and ceramics, which we experience now. The primary goal was always to develop and apply materials that are better for a specific purpose, with the term ‘better’ being applicable to any kind...
of property, be it mechanical, electrical, optical, or anything further.

While for traditional applications very efficient and economic materials have been found, new technological developments require properties that are not fully covered with the existing ones. For example, flexible electronics require materials that have electronic properties like semiconductors or metals, while at the same time being mechanically flexible and robust [1]. Construction, personal protection, aeronautics and similar fields require materials that are mechanically strong and tough like ceramics, but at the same time lightweight like polymers. Such demands posed a completely new challenge to materials research and design over the past years and decades. It became obvious that for many organic or inorganic materials the improvement of properties is meanwhile only incremental and involves finetuning of the dimensions, from the macroscopic to the nanoscopic scale, or structuring.

On the macroscopic scale, composite materials were introduced in order to meet the need for mutually supporting properties of the components. Reinforced concrete is one of the most prominent examples where the rather low ductility and tensile strength of cement is compensated with steel, which adds ductility and tensile strength to the final composite [2]. Without this development construction of tall buildings would not have occurred. In nature, a similar concept can be observed. Bone or nacre, for example, consist of proteins and minerals in specific structure and composition, making them extraordinarily strong, hard or tough, which was essential for the survival of the specific life-form producing it [3].

A translation of the concept from a macroscopic scale to micro- or nanoscopic scales comes along with the introduction of the term ‘hybrid materials’. Even though there is no exact definition of the term, it typically refers to blends of materials from different materials worlds where each of the components can contribute to the overall performance of the resulting material in a beneficial way. The main goal is to find materials that cover the properties gaps between the worlds of ceramics, metals, polymers and organics in general.

Many of the desired property combinations are important for future technological applications and range from wetting properties, optics, electronics towards construction or corrosion prevention. In many fields industrial processes are well established, thus methodologies that are compatible to the current ones, or can be incorporated with minimal invasion into current fabrication routes, are of great interest. Vapor phase processes play a crucial role within the spectrum of methods, since a great number of processes nowadays rely on vapor phase coating processes. Therefore, routes for designing hybrid materials from the gas phase are of immense interest for the industry, regardless of the application field.

In this paper the rather young field of vapor phase processing, with the goal to create functional hybrid materials, is overviewed. We are summarizing the most important achievements of recent and ongoing research in the fabrication and evaluation of hybrid materials for a variety of applications. Mechanical properties play a crucial role within the concept of hybrids, since the organic or polymeric component within a hybrid is considered most promising to add value to the mechanical properties of the resulting material. Therefore, the first part of the review will cover the most important achievements within that area. The forthcoming sections will overview the effects of hybridization of materials on their electronic, optical and biochemical properties. Further individual contributions to emerging fields will be discussed in the last part of the review.

2. Materials and methodologies

The fabrication of hybrid materials by means of vapor phase processes is very manifold and the routes rely on a plethora of growth methodologies. Among the most prominent techniques are those that base on the principle of atomic layer deposition (ALD) and involve modifications of the technique to enable treatment of organic materials. ALD is a coating technique that in principle bases on chemical vapor deposition (CVD), but is characterized with a different procedure of supplying the reactive chemicals to a substrate, namely a sequential exposure and purge processing of two or more gaseous precursors, which allows to grow thin films on a substrate with extreme thickness control and in a non-line-of-site fashion [5, 6]. In brief, during a conventional ALD process, the substrate to be coated is placed into a vacuum chamber and exposed to reactive precursor from the gas phase. The precursor binds to any available surface site of the substrate through chemical bonding until the whole surface is saturated with a maximum of one monolayer of the reactive precursor, which is typically a metal organic or organometallic reactant. After purging the excess precursor, the substrate is exposed to a counter precursor, typically water vapor, oxygen, ozone or similar, which converts the chemisorbed precursor into a layer of the desired coating and restores the surface functionality for the next cycle. Note that the two (or more) precursors are never present at the same time in the chamber. Their temporal separation is critically important to avoid a film growth in CVD fashion. Most characteristic of ALD is the self-saturation of the substrate after each precursor exposure and the linear growth of the film as a function of the number of cycles, which makes this technique extraordinarily interesting, especially in cases where very low dimensional coatings are required. However, ALD was initially developed for the deposition of inorganic thin films, thus an organic counterpart had to be introduced. Molecular layer deposition (MLD) bases on the same principle as ALD, but instead of reactive, metal containing precursors, functional organic monomers are used. As a result, a thin polymeric film is grown with its thickness being a function of pulse, exposure and purge cycles. Consequently, a combination of ALD and MLD will result in a hybrid material growing as a function of the number of processing cycles [7, 8].

The most prominent family of such films are metal alkoxide polymers, grown from organometallic precursors and alcohols. These hybrid films are called ‘metalcones’ with reference to the silicones which show a rather similar molecular composition. Depending on the metal involved, the term ‘metalcone’ is altered accordingly.
The ALD process technology has also inspired the development of another process called vapor phase infiltration (VPI) [8, 9]. The processing procedure is very similar to ALD, but instead of applying an inorganic coating to an inorganic substrate, polymeric substrates are targeted. Given that a polymer shows molecular mobility and porosity, it can be considered as a very viscous liquid. The precursor vapors from the gas phase can therefore not only bind to the surface of the polymer, but also dissolve into the substrate. An in-diffusion of metal containing precursors into a polymeric substrate and a reaction with functional sites of the polymer or entrapping of the metal or metal oxide inside the polymer brings about a hybridization of the inorganic infiltrate with the polymeric matrix. This process has numerous facets both in the setup as well as in the choice of substrate materials, which resulted in the baptismation of the process in a variety of ways. The reader might encounter multiple pulsed vapor phase infiltration (MPI), sequential vapor infiltration (SVI) or sequential infiltration synthesis (SIS), which essentially mean the same procedure with slight processing differences. In all cases, the inorganic infiltrate is generated in a subsurface area of a polymer and through more or less strong chemical or physical bonding results in a hybrid material with improved or at least modified properties in comparison to the initial polymer.

In contrast to ALD, CVD relies on a simultaneous supply of molecules to the reactor. In this way the reaction is not limited to surface reactions on the substrate but can occur in the gas phase above the substrate and deposit. Often the reactions between the precursors require higher activation energies than it is the case with ALD, thus activation of the process is often needed. The activation might occur in various ways, either traditionally with elevated temperatures, or with an energy supply through a plasma, which is then called plasma enhanced CVD (PECVD) [10]. Initiated CVD (iCVD) is yet another methodology that showed great promise for the fabrication of hybrid materials. The technique transfers the mechanistic understanding of wet chemical polymer synthesis to the vapor phase. The polymerization is induced by radicals, therefore the process involved free radical generation and a stepwise growth of the polymer chain. Typically, a volatile initiator is introduced into the process chamber along with one or more types of monomers. A key step is in most cases the thermal decomposition of the initiator, commonly achieved with a heated filament array inside the vacuum chamber. The filaments drive the pyrolysis of the initiator while allowing the substrate to remain cold enough to promote the adsorption of the monomers required for the polymer film growth. A similar procedure is applied in oxidative CVD (oCVD), where instead of an initiation of the polymerization with a radical the substrate is formed by simultaneous introduction of an oxidant and the monomer [11].

Besides the mentioned methods, researchers constantly develop new ones or modify existing ones, which will be shortly mentioned in the respective parts of this paper and the reader is encouraged to further read the original contributions for details about the processes.

3. Mechanical properties

Natural and synthetic polymers play a key role in various branches of engineering including biomedical, optoelectronic, electrochemical and environmental engineering [12]. In terms of mechanical properties, most polymeric materials typically exhibit high elongation values, but have a low toughness. One possible workaround involves the incorporation of metals that bind to the polymer backbone. This can be achieved either wet chemically, during the polymerization, or subsequently, by various gas phase techniques. The resulting hybrid material contains covalent bonds between the polymer chains and the infiltrated metal, which often improves the mechanical properties of the hybrid in comparison to the initial polymer.

3.1. Mechanical properties of polymers, modified by vapor phase infiltration (VPI) techniques

3.1.1. MPI (VPI) of biopolymers. In 2009, Lee et al [13] showed the first example of vapor phase infiltration (there: multiple pulsed vapor-phase infiltration—MPI), which resulted in greatly enhanced mechanical properties of natural dragline spider silk. Al2O3, TiO2 or ZnO were incorporated into the polymeric structure applying a slightly modified ALD process in which the metal precursors were infused into the biopolymer. As a result, the Young’s modulus of the silk was increased from 9.7 GPa to 53–68 GPa and 53–66 GPa after Al and Ti infiltration, respectively. The reaction mechanism of the vaporized precursors with the biopolymer played a critical role in the experiment. The authors found that a cleavage of the hydrogen bonds between the polymeric chains in the crystalline portions of the silk by infiltration with water vapor played a critical role for the alteration of the mechanical properties [14]. The subsequent reaction and saturation of the exposed functionalities with the metal–organic precursor resulted in the formation of Me-O bonds in the polymer bulk. This, in turn, led to cross-linking and to a decrease of the degree of protein crystallinity (figure 1).

A similar reaction was observed by the same group [15] in a subsequent work, where the VPI process was applied to natural collagen membranes. Al2O3, TiO2 or ZnO, infiltrated into dried collagen membranes, significantly improved their mechanical properties, increasing their modulus of toughness 3-fold (figure 2). The interesting fact in both mentioned cases was that both stress and strain of the initial biopolymer were increased, an observation which does not reflect the typical behavior of polymers upon cross-linking.

Another biopolymer, cellulose, was also modified in a similar way. Gregorczyk et al showed that after infiltration of trimethylaluminum (TMA) or diethylzinc (DEZ), the biopolymeric fibers exhibit a change in their mechanical properties [16]. The resulting tensile strength of the cellulosic fibers turned out to be dependent on the total number of infiltration cycles and the precursor used. In the best case it was nearly doubled from ~160 MPa to ~260 MPa after only four infiltration cycles with DEZ. A great increase was also observed.
3.1.2. MPI (VPI) of synthetic polymers. The greatly improved mechanical properties of the aforementioned biopolymers triggered the application of the same process to synthetic polymers. However, an analogous increase in both stress and strain, as in the case of natural fibers, was not observed.

Lee et al [17] demonstrated successful infiltration of polytetrafluoroethylene (PTFE) with Zn, despite the fact that PTFE is largely physically and chemically inert. Both the mechanical properties and the polymer structure of PTFE were altered. In agreement with DFT calculations, the spectroscopic data showed the presence of Zn–O–Zn bonds that crosslinked the polymeric chains. A side reaction, an incorporation of Zn into the PTFE C-F bonds, was eliminating the defect sites of the original fiber. As a result, the mobility and flexibility of PTFE chains were limited, which also limited the extensibility, but increased the tensile strength of the polymer twofold.

After applying an alumina VPI process, Sun et al reported a significant impact of the interfacial polyamide 6 (PA6)-inorganic hybrid layer on the Young’s modulus and the hardness of the material [18]. Nanoindentation showed that the PA6-Al hybrid layer can absorb the energy released upon crack formation, thus preventing further crack propagation. Akyildiz et al [19] investigated the influence of process temperature and exposure time on the hybrid layer formation in PA6 in more detail.

Besides PA6, polypropylene (PP) and Pellethane were coated and infiltrated with Al$_2$O$_3$ to target the mechanical properties enhancement [20]. Both, short and long precursor doses led to subsurface and surface modifications of the polymers, which directly impacted the mechanical response of these polymers, including the Young’s modulus and the failure strain. The ALD treatment increased the Young’s modulus of the polymers during the first $\sim$200 ALD cycles. Thicker coatings did not make any changes to the modulus, but mainly embrittled the polymer, suggesting that the significant mechanical changes are mainly determined during the initial deposition cycles.

The possible reaction mechanisms and reactivity of TMA vapor with the ester, amide, and carboxylic acid functional groups of poly(methyl methacrylate) (PMMA), poly(vinylpyrrolidone) (PVP), and poly(acrylic acid) (PAA), respectively, were demonstrated by Hill et al [21]. Although the mechanical properties of these hybrids have not been characterized, the insight may help to predict the chemical interactions occurring during vapor phase infiltration, thus helping to design hybrid materials.

The thermodynamics and kinetics of sequential infiltration synthesis (SIS), a further naming of VPI, was described by Waldman et al [22]. The authors discussed the various experimental and theoretical methods that may expand the current database of SIS-fabricated hybrid materials.

The influence of the crystallinity of a polymeric substrate on the infiltration degree was studied by Padbury and Jur [23]. The authors infiltrated aluminum oxide into various polyethylene terephthalate (PET) fibers with different crystallinity and observed that precursor penetration into the substrate in the elastic modulus after infiltration of DEZ. In contrast, an infiltration with TMA had only minor impact on the mechanical properties of the cellulose. Based on XPS and Raman spectroscopic investigations, the authors proposed a reaction scheme in which both precursors crosslink cellulose chains, but also attack the glucose backbone, causing ring opening reactions. This degradation reaction weakens the cellulose fibers and TMA, which is a stronger Lewis acid than DEZ, more efficiently attacks the ring structure, thus resulting in a more rapid degradation of the mechanical properties of the cellulose.

![Figure 1](image1.png)

**Figure 1.** Schematic description of the proposed molecular changes in the silk, induced by MPI (VPI). From [13]. Reprinted with permission from AAAS.

![Figure 2](image2.png)

**Figure 2.** Deformation behavior of metal-infiltrated (Al, Zn and Ti) collagen membranes (CM) under the uniaxial tensile test. Inset: SEM image of a Ti-infiltrated (CM/TiO$_2$) membrane. Reprinted with permission from [15]. Copyright (2010) American Chemical Society.
was less effective for more crystalline polymers (figure 3). Accordingly, the improvement of the mechanical properties was directly correlated with the degree of crystallinity.

Dusoe et al. (2024) obtained hybrid nanopillars with an exceptional modulus of resilience per density of ~13.4 kJ kg\(^{-1}\) by applying VPI of aluminum oxide to a lithographically patterned photoresist SU-8 (figure 4(a)). The nanomechanical measurements showed a unique combination of mechanical properties: metal-like strength (~500 MPa) and an unusually low, foam-like Young’s modulus of ~7 GPa (figures 4(b), (c)). All above makes this material superior to most known engineering materials.

Besides improved mechanical properties, VPI-treated polymers have shown improved stability as well. Azpitarte et al. (2025) have shown that ZnO-infiltrated Kevlar fibers become more resistant against thermal and UV-radiation induced degradation (25). The investigated ZnO-Kevlar hybrid had a higher thermal degradation temperature while at the same time the infiltrated ZnO absorbed UV light and in this way suppressed a UV-induced degradation of the polymer. The infiltration of ZnO generated a highly cross-linked functional subsurface layer in the Kevlar fibers, which was key for the enhanced stability and mechanical properties of the polymer.

3.2. Mechanical properties of hybrids, grown by atomic and molecular layer deposition (ALD/MLD)

3.2.1. Metalcone thin films. The elastic modulus and hardness of hafnicone films were measured by nanoindentation, resulting in values of 47 GPa and 2.6 GPa, respectively (26). For comparison, inorganic ALD-deposited HfO\(_2\) films showed an elastic modulus of 220 GPa and a hardness of 13 GPa. The elastic modulus of the hafnicone film is in the same order of magnitude as the elastic moduli of further metalcone films. Alucone films, for example, have an elastic modulus of 21 GPa (27), while in the case of titancone the values depended on the used organic precursor. With glycerol 30.6 GPa were obtained and with ethylene glycol only 8.0 GPa (28). The spread of values demonstrates that hybrid metalcone thin films can be a toolbox for designing hybrid films with tunable properties by either altering the size of the organic moieties in the hybrid structure or by changing the metal and thus the quality of the backbone cross-linking.

3.2.2. Hybrid coordination network (CNs) thin films. Inorganic–organic coordination network materials (CNs), such as metal–organic frameworks (MOFs), combine inherent properties of inorganic cations and organic building blocks to provide crystalline porous structures. CNs show good potential for applications in various fields and are exceptional materials for their thermal and mechanical stability.

Well-crystalline calcium terephthalate (Ca-TP) coordination network thin films were grown by ALD/MLD, as reported by Ahvenniemi and Karpinen (29). The authors investigated the mechanical properties for both dry and water-intercalated films. After exposure to humid air, the Ca-TP thin film samples were found to withstand elongations on ~23% before breaking, while the respective dry Ca-TP films broke already at ~1.5–2.0% elongation (figure 5). However, even the dry Ca-TP films showed good elasticity upon induced tensile stress. The outcome appeared surprising to the authors, as they expected a rather similar behavior, but such a significant difference in the performance was found to be appealing for a further design and tailoring of the mechanical properties of such hybrids.

3.3. Mechanical properties of hybrids, grown by plasma enhanced chemical vapor deposition (PECVD)

The mechanical properties of hybrid thin films, deposited by plasma enhanced chemical vapor deposition (PECVD), were also investigated (30, 31). The films were grown with thiophene and tetrathoxy silane TEOS and the deposition was carried out under varying processing conditions including different annealing temperatures or RF (radio frequency) plasma power. The results showed that the hardness and Young’s modulus of the hybrid films increased along with an increased plasma power. This indicated that the plasma power had a direct impact on the density and crosslinking yield. Besides, the hardness and the Young’s modulus decreased for annealing temperatures below 400 °C, indicating that the films became more porous at lower temperatures, likely because of residual CH\(_3\) moieties.

![Figure 3. Mass uptake behavior of TMA in PET polymer films with different crystallinities. In-situ QCM mass uptake of ten consecutive multidoses of TMA in PET at 100 °C using an ALD cycle sequence with an eliminated water dose. Reprinted from [23], with the permission of AIP Publishing.](image-url)
Figure 4. (a) SEM micrographs of the in-situ nanomechanical testing tip over arrays of Al$_2$O$_3$-infiltrated SU-8 nanopillars (false-colored) and the magnified view of an individual nanocomposite SU-8 nanopillar (inset). (b) Measured $\sigma$-y and (c) E of SU-8 nanopillars with respect to the number of applied Al$_2$O$_3$ infiltration synthesis cycles. Reprinted with permission from [24]. Copyright (2017) American Chemical Society.

Figure 5. Elongation test results for Ca-TP films on a polyimide substrate. The illustration panels on the top and middle describe the expected force-to-elongation graphs for thin-film + thick-substrate systems: in panel (1), only the substrate’s elongation profile is initially seen; then, the breakage of the thin film is seen as a small but sharp drop in panel (2) before the breakage of the substrate later on in panel (3). Bottom graphs show experimental elongation curves for representative Ca-TP thin film samples; the thin-film breakage is visible in the force curves (a) for the trihydrated films and in the derivative curves (b) for the dry films. Reprinted with permission from [29]. Copyright (2016) American Chemical Society.

4. Gas-phase deposited hybrids for electronic applications

One of the recent and very quickly expanding fields, which can significantly benefit from hybrid materials, is electronics. Organic-inorganic hybrids promise a merger of the properties of conventional silicon-based semiconductor devices with the ability to be bent, stretched or compressed without significantly compromising the functionalities. Such synergistic properties are vital for the development of wearable and foldable electronics, biomedical sensors for digital medicine, organic light-emitting diodes, low-power energy sources, or
non-volatile memory applications. The great controllability of the gas-phase deposition processes allows for precise tuning of the electronic and mechanical properties of the hybrid. Many factors such as the dielectric constant, band gap, mobility, carrier concentration, etc., can be adapted by tuning the concentration ratio of the organic to inorganic parts. The easy scalability of the vapor-phase deposition techniques towards industrial scale, the purity of the formed structures and the true chemical interaction between the organic and inorganic constituents make gas phase methods highly attractive for the development and integration of novel hybrid materials into devices. However, it is a young and growing field, and for some applications only proofs-of-concept have been shown. Moreover, there are no or very few reports on hybrid materials with certain properties including piezoelectric, pyroelectric, ferroelastic, superconducting, or ion-conducting properties of materials synthesized by gas-phase methods. Taking into consideration all the benefits which hybrid materials can bring into the field of flexible electronics, there is a high demand for active research to fill this gap.

4.1. Dielectrics

One of the key challenges in the development of novel organic thin-film transistors (OTFT) is the need for a high-performance dielectric layer, as it has a direct impact on the TFT’s characteristics such as carrier mobility ($\mu$), operation voltage, and power consumption. It is beneficial to keep the capacitance density as high as possible in order to achieve a low power consumption in OTFTs. This can be achieved by increasing the dielectric constant ($k$-value) of the dielectric layer or by reducing its thickness. Hybrid organic-inorganic films are promising as the gate dielectric of low-voltage operating organic thin-film transistors. Namely, by changing the amount and ratio of the organic and inorganic components, it becomes possible to tune the high-$k$ and high dielectric strength (leakage resistance). Besides, the improved mechanical properties of the hybrids make them especially attractive for flexible electronics.

Due to the well-known dielectric properties of zirconium oxide, Zr-based hybrids are promising materials for applications in OTFT. Zirconium belongs to the group of metalocene hybrids and form as a result of reactions between zirconium tetra-t-butoxide and an organic diol. The group of S. George utilized zircon as the dielectric layer in pentacene-based OTFTs [32]. Zircones were grown from zirconium tert-butoxide (ZTB) and ethylene glycol (e.g.) as precursors at temperatures between 105 °C and 195 °C. These films were stable in air and showed a high field-effect mobility of 2.11 cm$^2$ V$^{-1}$ s$^{-1}$ operating at −3 V with an on/off current ratio of $\sim 10^7$. The leakage current of the zirconate hybrid was $\sim 5.6 \times 10^{-7}$ A cm$^{-2}$, which is two orders of magnitude better than that of a pure ZrO$_2$ ALD film, being $\sim 2.7 \times 10^{-5}$ A cm$^{-2}$. At the same time, the carbon constituents lowered the dielectric constant from 16 for the ZrO$_2$ film to 6.7 for the zirconate film. These results demonstrate the applicability of MLD-grown zirconate films as gate dielectric materials.

Aluminum oxide is another widely used inorganic dielectric with $k \sim 9.0$, and therefore, aluminum-based hybrids are potentially good candidates for a use in OTFTs. Cheng et al. studied hybrids of self-assembled MLD-deposited octetyltri-chlorosilane (OTS) layers and Al$_2$O$_3$ linkers deposited from (TMA)/H$_2$O by ALD [33]. The inorganic Al$_2$O$_3$ layer bridged the neighboring OTS through O-Si bonds. XPS and electrical characterization of the hybrid laminates revealed that their band gap and dielectric constant were tunable from $\sim 7.00$ to 6.09 eV and $\sim 9.0$ to 4.5, respectively. To investigate the dielectric properties of the ALD-MLD hybrid, a dual-gated MoS$_2$ field-effect transistor was synthesized with sub-10 nm OTS−Al$_2$O$_3$ applied as a top-gate dielectric. The hybrid MoS$_2$ transistor showed promising dielectric properties including a low leakage current density of $\sim 1 \times 10^{-6}$ A cm$^{-2}$ at 1 MV cm$^{-1}$ and a small hysteresis of $\sim 50$ mV in the transfer characteristics. Therefore, OTS−Al$_2$O$_3$ hybrids show promise for dielectric applications for 2D material-based devices. However, the n-type transistor behavior of MoS$_2$ changed upon application of the OTS−Al$_2$O$_3$ dielectric. The threshold voltage ($V_{th}$) shifted positively by $\sim 4.1$ V, which indicated a p-doping effect which was explained by the presence of interface-trapped charges from H$_2$O or O$_2$ adsorbates during the MLD of OTS, whereas ALD oxides usually tend to introduce negative $V_{th}$ shifts [34].

Due to the large amount of hydroxyl (-OH) functionalities, an adverse effect can also be observed on ALD-deposited metal oxide surfaces. The hydroxyl groups may form unwanted trap sites at the dielectric-semiconductor interfaces [35]. The high charge trap density leads to a drop in device performance, including a reduction of the charge mobility, appearance of hysteresis, and shifting of threshold voltages. Seong et al [36] introduced an organic passivation on ALD-deposited Al$_2$O$_3$ with non-polar moieties to minimize the interfacial trap density. A polymer film was deposited by iCVD using 1,3,5-trimethyl-1,3,5-trivinyl cyclotrisiloxane (V$_3$D$_3$) and tert-butyl peroxide (TBPO). A metal-insulator-metal (MIM) device was fabricated to measure the capacitance of the 15 nm thick hybrid structure (figure 6). The capacitance of the hybrid was tuned from 100 to 450 nF cm$^{-2}$ by changing the thickness ratio of Al$_2$O$_3$:pV$_3$D$_3$. Through the values of C$_t$ and the total thickness of the layers, the $k$ values of the hybrid were estimated to range from 3.11 to 5.66, which is substantially higher than the $\sim 2.2$ of a pure pV$_3$D$_3$ layer. Even though higher values of C$_t$ are usually preferred to induce a higher carrier density, without passivation of the polar surfaces the accumulated charge carriers will be consumed to fill the deep surface traps, which lowers the TFT performance. The enhancement of the overall device performance and the long-term operation stability was proven with a constant voltage stress test for 3000 s. Moreover, the 15 nm-thick hybrid TFT was able to withstand the tensile strain up to 3.3%, strongly outperforming the mechanical flexibility of the pure Al$_2$O$_3$ layer. However, the hybrid also exhibits some drawbacks of both the involved organics and inorganics. Among the most critical ones are the existence of trapping sites in the Al$_2$O$_3$ layer and a noisy leakage current at continuous bias stress. The authors [36] concluded that the observed hard breakdown in
the Al$_2$O$_3$ layer can be ascribed to the presence of polar – OH groups in the oxide insulating layers, which act as trapping sites. The authors of this review assume that the high surface roughness and surface area of the gold contacts of the MIM device might contribute to the number of trapping sites and therefore enhance the leakage current density. From electrical studies it is known that roughness at the metal/insulator interface enhances the electromagnetic field at spike defects. The effect is higher with an increase of the height to thickness ratio of the spike, whereas the results of [36] show no spiky defects. However, a high-quality surface of the contact is needed for an accurate study of the dielectric layer performance.

While purely inorganic films may loose the accumulated charge due to interfacial trap density linked to the presence of the surface hydroxyl functionalities [33], purely organic films often suffer from their air sensitivity. Zhou et al demonstrated a highly stable hybrid film consisting of MLD-deposited TMA and p-phenylenediamine (PPD, C$_6$H$_4$(NH$_2$)$_2$) after alloying with inorganic ALD-deposited Al$_2$O$_3$ [37]. The initial MLD film thickness increased by 30% after 300 h of exposure to air, while the hybrid MLD/ALD alloy showed less than 5% thickness change even after tens of weeks. Moreover, the alloyed ALD/MLD hybrid showed promising dielectric properties, such as a leakage current density of $\sim 2.3 \times 10^{-8}$ A/cm$^2$ at an electric field of 1 MV cm$^{-1}$ and a dielectric constant around 6.2.

For implementing hybrids into real electronic devices, development of mechanically durable and flexible materials is essential. In order to overcome this issue, a novel homogeneous gate dielectric with sub 5 nm equivalent oxide thickness was demonstrated by Kim et al [38]. In a one-step deposition by iCVD they obtained AlO$_x$-grafted poly(2-hydroxyethyl methacrylate) dielectrics (pHEMA-g-AlO$_x$) from 2-hydroxyethyl methacrylate and TMA. The obtained hybrid had a $K$ value of $\sim 7$ and a leakage current density of less than $3 \times 10^{-7}$ A/cm$^2$ at 2 MV cm$^{-1}$. A smooth tuning of the dielectric characteristics such as, dielectric constant, leakage current density, and electrical breakdown field strength of the hybrid was possible by adjusting the concentration of Al in the organic-inorganic film. The excellent dielectric performance was maintained even under a tensile strain of up to 2.6%, whereas a MIM device with Al$_2$O$_3$ only had a breakdown at a strain above 1.0%, which resulted from the enhanced flexibility of the polymeric matrix (figure 7). The device performance of pHEMA-g-AlO$_x$ showed excellent dielectric properties compared to existing hybrid and organic materials, but at the same time, improved mechanical properties. All above-mentioned makes the iCVD hybrid promising for a high-performance and low-power operation of flexible electronics.

Nowadays, thin-film high-$k$ dielectrics are widely implemented in charge trapping memory (CTM) capacitors, non-volatile memory devices that are able to retain stored information in the absence of power. CTM defines the program/erase states via supplying charges to and draining charges from the charge-storage layer, respectively, similar to a floating-gate memory. In CTM, charges are spatially distributed due to the localization of the traps in the bandgap of the charge-trapping layer. The use of high-$k$ dielectrics makes downsampling of the cell size possible, since high-$k$ dielectrics can possess a thicker physical thickness than SiO$_2$ for the same equivalent oxide thickness (EOT).

One of the examples of utilization of hybrid materials in charge trapping memory capacitors was shown by Cao et al [39]. Inorganic TiCl$_3$ and fumaric acid (FA) were used as precursors for an MLDBased hybrid. In order to verify the charge trapping ability of the hybrid, the authors fabricated a flash memory capacitor structure that consisted of a top electrode, blocking oxide, charge trapping layer, tunnel oxide, and a p-Si substrate. All layers, except for the Pt top electrode, were continuously deposited by vapor deposition methods in an ALD reactor without breaking the vacuum, which is a great advantage for manufacturing. The charge-storage ability improved with the thickness increase of the Ti-based hybrid. The 10 nm thick sample showed the largest memory window of 8.01 V when the sweeping gate voltage was ±14 V, indicating a good charge-storage capability.

More recently, the same group studied the influence of the cis- and trans-configurations of the organic butenedioic acid precursor on the characteristics of the resulting device. For that, they substituted FA (trans-butenedioic acid) with its isomer MA (cis-butenedioic acid) [40]. They conducted a systematic comparison of Ti–MA and Ti–FA regarding growth, stability, and charge trapping ability. From the capacitance–voltage (C–V) curves of the sample with 7 nm Ti–MA hybrid film it can be seen that the Ti–MA hybrid-based memory cell exhibited a much larger memory window than the Ti–FA memory cell (figure 8(a)). Moreover, the Ti–MA hybrid exhibited very good endurance and stability in air; the charge trapping ability could withstand 100 d of exposure to the ambience with a shrinkage of its memory window by only 12.6% (figure 8(b)).

4.2. Conductive hybrids

Conductive and flexible films are crucial for many emerging applications, including displays, wearable devices, personal medical devices, photovoltaics, etc Numerous research groups are investing their efforts into achieving highly conductive hybrid organic-inorganic materials, which at the same time maintain their mechanical flexibility.

Zinc oxide is considered to be the most promising substitute for the conductive and transparent In$_2$O$_3$. However, the intrinsic brittleness of inorganic oxides hampers their use in flexible applications. The group of S. George investigated a zincone hybrid, which is closely related to a ZnO film and, therefore, may combine the conductivity of ZnO with the flexibility of an organic layer [41]. They employed DEZ, hydroquinone (HQ) and water to perform MLD-ALD films. The reaction between DEZ and HQ generates a molecular chain in the form of $(\sim$Zn-O-phenylene-O$\sim)_{n}$, which is an electrical conductor. Measurements of a pure ZnO ALD film showed a conductivity of $\sim$14 S m$^{-1}$, while the ALD:MLD alloy showed $\sim$170 S m$^{-1}$, demonstrating a considerable enhancement of the conductivity in the hybrid alloy of more than one order of magnitude (figure 9). Authors explained
the conductivity enhancement with a higher electron mobility, which is caused by the electron coupling of the delocalized π-electrons from the conjugated phenylene rings in HQ and the neighboring ZnO clusters. At the same time, the ZnO layer can provide a high density of charge carriers caused by oxygen vacancies in the ZnO layer. The conductivity values of the zincone/ZnO alloys outperformed that of inorganic zinc oxide and are largely comparable with high temperature
the origin of the enhanced conductivity of the 2:2 alloy, compared to the 1:1 alloy, was not clearly stated, but the values reached 170 S cm⁻¹ and 116 S cm⁻¹, respectively. However, it may be speculated that one DEZ/H₂O ALD cycle may not be sufficient for the formation of a continuous monolayer due to steric effects of the precursors or the limited amount of available active sites, whereas the application of a second ZnO ALD cycle could complete the monolayer and therefore significantly increase the conductivity. Moreover, optical measurements proved high transparency of the hybrids in the visible range. Such zinccone:ZnO alloys are promising candidates to replace ITO in displays and photovoltaic devices.

However, zinccone films can be unstable in ambient conditions due to their micro-porosity, which might reach 1.2 vol% in as-deposited films [42]. Upon environmental degradation, the porosity of the hybrid can increase to 39 vol%. Altering the number of ZnO ALD and MLZ zincone layers within hybrid alloys with a theoretical formula (ZnO)ₓ(Zn–O–C₆H₄–O)ₘ allowed to control and suppress the micro-porosity of the hybrids. It was shown that a periodic multilayer with a = 10 is already environmentally stable, and with the number of ZnO layers a ≥ 20 a similar resistivity to that of purely inorganic ZnO was observed.

Conductive polymers are prominent materials for substituting inorganics in a broad range of electronic devices. They are investigated for several decades. Much of the research focuses on improving their conductivity and thermal stability. Commonly, the conductivity of such polymers can be enhanced by doping. However, a typical doping process is done in wet chemical ways, which can introduce impurities and influence the morphology and crystallinity negatively. W. Wang et al demonstrated a novel and promising approach for doping conductive polymers without wet chemistry [43]. The authors performed vapor phase infiltration of DEZ and H₂O into polyaniline (PANI) substrates, which induces the growth of ZnO in the subsurface of the PANI. An infiltration of DEZ results in binding of Zn to the nitrogen present in the polymer backbone, which consequently induces Lewis acid type doping of PANI. At the same time the subsurface grown ZnO particles become doped with nitrogen. Moreover, the interpenetrated structure further provides additional conduction pathways through cross-linking of the polymer chains with the inorganic moiety. Such synergistic mutual doping results in a high conductivity of the hybrid being ~18.42 S cm⁻¹, which outperforms the wet chemically HCl-doped PANI by more than two orders of magnitude.

Application of further metal halides, such as MoCl₃ or SnCl₄, as VPI dopants for polyaniline, resulted in significant enhancements of conductivities by up to six orders of magnitude [44]. Besides the enhanced electron mobility along the polymer chain, the hybrid was stable at elevated temperatures and conductivity was barely affected even after thermal treatment at 150 °C. This approach can also be extended to further conductive polymers. For example, doping of poly(3-hexyl) thiophene (P3HT) with MoCl₃ was recently demonstrated to be similarly efficient [45].

4.3. Triboelectric and thermoelectric hybrids

Triboelectric nanogenerators (TENG) can also benefit from hybrid materials. The working principle of TENG devices is based on converting mechanical energy into electrical energy, which can be achieved by building an interface between two materials with different electronic affinity. TENGs opt for a broad application range, including wearable electronics, charging batteries, activators of chemical reactions, etc. However, in order to generate, TENGs require friction between the triboelectric materials which causes wearing of the surfaces. Therefore, modification of not only the surface, but also the bulk of the materials promises much better functionality and durability. Yanhao Yu et al applied SIS of Al₂O₃ on various polymers, including polydimethylsiloxane (PDMS), polyimide (Kapton), and poly(methyl methacrylate) (PMMA) [46]. As a result of the infiltration, the Al₂O₃ moieties penetrated these polymers by at least 3 µm. The electron attaining capability of such doped polymers was significantly reduced due to the strong repulsion of electrons by Al₂O₃. The combination of infiltrated and pristine polymers allowed to create high-performance TENG devices. But unlike a pure surface modification, which is commonly applied to tune TENG performance, the SIS process allowed to overcome wearing of the surfaces of the triboelectric devices, as SIS doping changed the properties of the bulk of the polymer. The SIS doping strategy appears to be a promising top-down approach to tune the efficiency of polymeric electronic devices.

An intriguing filed of application of hybrid materials is thermoelectricity. Thermoelectric energy can be harvested on different scales, from the human body temperature to high-temperature industrial processes. The use of thermoelectricity not only increases the efficiency of the existing technologies but also gives a boost to the development of entirely new ones. Thermoelectricity is a key to realizing self-powered electronic applications, like low-power operating wearable electronics.
and biomedical sensors. Applying hybrid materials for thermolectric generators will provide enhanced flexibility, which is crucial for wearable devices. The most significant development of thermolectric hybrid devices relies on ZnO, as it is a transparent semiconductor with the carrier concentration being controllable by visible light and it has promising thermolectric properties. Layering it with organic materials should allow tuning of its thermolectric properties due to an enhanced phonon scattering and charge confinement.

Tynell et al fabricated ALD-MLD hybrid superlattices consisting of hydroquinone (HQ), 4-aminophenol (AP), 4,40-oxcyaniline (ODA) and ZnO [47]. The ZnO:organic layer ratio was varied between 199:1 and 39:1, and an increase in the carrier concentration was achieved for lower fractions of organic layers in the resulting multilayered structure, while higher organic contents lead to considerable reduction of the carrier concentration. Overall, HQ and ODA had similar effects on the ZnO-based transport properties in the hybrid, but the impact of AP on both the Seebeck coefficient and the resistivity appeared to be very low.

In purely inorganic films, an enhancement of electrical conductivity of inorganic ZnO can be achieved with Al-doping. Such an approach is also efficient for the mentioned hybrid MLD ZnO-hydroquinone systems. The organic layers are beneficial for blocking phonon transport, but at the same time they lower the carrier concentrations [48]. Thus, an inclusion of aluminum co-doping enables to offset the undesired effect and keep the transport properties of Zn1−xAlxHQ2O (with x values of 0−0.02) essentially at the same level as those in inorganic Al-doped ZnO.

The possibility of growing the above-described Al-doped ZnO-hydroquinone superlattices by ALD/MLD directly on flexible cotton textile substrates was demonstrated by the research group of Maarit Karppinen [49]. Since cotton is the most widely used natural fiber cloth, applying electrically conductive materials to it is a natural approach for fully integrated wearable electronic devices. Besides the conductivity and good thermolectric properties of the as-deposited materials, the hybrid superlattices on cotton substrates showed an enhanced resistance to mechanical strain (figure 10(a)). For a mechanical durability test of the hybrids, the coated cotton textiles were folded twice. After that, they were rolled to a compact roll. The resulting resistance of the bent samples increased by 123% and 218% for the inorganic films (ZnO)100 and (Al2O3)30(ZnO)60, while in the case of the hybrid (Al2O3)30(ZnO)58(HQ)12 superlattice, the mechanical treatment increased the resistance by only 21%. Apparently, the presence of organic layers significantly improves the flexibility of the ZnO-organic conductive superlattice. In addition to the enhanced flexibility, the ZnO–organic superlattices showed remarkably lower thermal conductivities in comparison to pristine inorganic ZnO, thus suggesting a better thermolectric figure-of-merit.

In a later work, the same group fabricated and tested a prototype of a thin-film thermolectric device based on ZnO-benzene MLD films [50]. The organic layers suppress the thermal conductivity, which makes these hybrid structures more effective than pure ZnO ALD films (figure 10(b)).

The overall power output of such devices is in the mW range. However, there are routes to increase this value, namely by increasing the thickness or by fabricating thermolectric modules with a combination of both p-type and n-type materials. These first results appear very encouraging for further research in this field.

4.4. Magnetic materials

Organic magnets are a class of hybrid materials which have been studied for about 40 years. Such materials can display ferromagnetism, they have a low density, are transparent, and are electrically insulating. Besides, organic-based magnets show properties similar to inorganic magnets, including hysteresis with saturation and coercivity, but they do not require an energy-intensive metallurgical fabrication. In a best case, organic magnets may replace rare Earth-based magnets with Earth abundant magnets. The research in this field focused initially on magneto-resistive random-access memory (RAM) applications, but more recently studies stepped into spintronic devices, showing an important impact on the improvement of light-emitting diodes and transistors.

The critical temperature, or the temperature at which materials become magnetic, is a crucial characteristic. A very low critical temperature requires cooling of the system and constrains the real-life applications. Therefore, the development of the first known room temperature organic magnet formed by MLD is an important breakthrough [51]. Sequential pulsing of vanadium hexacarbonyl (V(CO)6) and tetracyanoethylene (TCNE) resulted in the formation of an MLD V[TCNE]:tetracyanoethylenelike nanolaminate. The coercivity of the MLD films was measured with superconducting quantum interference device (SQUID) magnetometer and reached ~80 Oe at both 5 and 300 K. However, the stability of the film in air was poor. The resistance of the hybrid films increased by 50% within a day of exposure to air. Nevertheless, the magnetoresistance data of the hybrid magnetic tunnel junction (MTJ) structure clearly showed the spin polarizing nature of the hybrid. With further research and development, novel spintronic devices may benefit from such hybrid organic-inorganic magnets.

The group of Arthur J. Epstein continued this research and investigated the formation of TCNE hybrids grown by MLD, with various metallic counterparts, including Co[TCNE]x and Co3Vx[TCNE] [52]. The Co[TCNE]x hybrid contained a significant amount of metallic cobalt in addition to cobalt oxide, which was shown with x-ray photoelectron spectroscopy. The magnetic hysteresis loops of the film showed a large coercive field of 450 Oe at 5 K and 40 Oe at 300 K. The large coercive field with anisotropy measured from the Co[TCNE]x sample is consistent with the magnetic metallic Co nano-disks identified in the film. The growth of Co3Vx[TCNE] film was achieved by alternately depositing V[TCNE] and Co/TCNE layers. The coercive fields for this hybrid were 50 Oe at 5 K and 30 Oe at 300 K. Interestingly, there was no metallic Co in the Co3Vx[TCNE] hybrid.

Recently, Liu et al demonstrated the applicability of V[TCNE]x hybrids for organic-based magnon spintronics, for
Figure 10. (a) Schematic illustration of an ALD/MLD-fabricated ZnO–organic superlattice which strongly scatters phonons in the superlattice cross-plane direction (the organic building block is benzene, resulting from the hydroquinone precursor). [49] John Wiley & Sons. © 2017 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. (b) V–T curves measured with a load in the circuit for devices deposited on PEN for ZnO layers with different thicknesses (100 nm yellow, 150 nm purple, and 500 nm green) and for a 100 nm thick ZnO:benzene layer (only in the case of the closed circuit with the load). Reprinted from [50], with the permission of AIP Publishing.

which the concept bases on using spin-wave quanta for transmission, processing, and storage of information [53]. The hybrid magnets are promising magnetic insulator candidates for a substitution of yttrium iron garnet as they possess both the reduced spin–orbit coupling and the lack of electron-lattice scattering, which is crucial for the small values of Gilbert damping. The authors observed resonantly generated magnons in the hybrid MLD films of V(TCNE)$_x$ and an efficient spin pumping by magnon scattering at the V(TCNE)$_x$/Pt interface. The extremely low values of Gilbert damping, comparable to those in yttrium iron garnet, and the synthetic versatility make this hybrid promising for magnon-current generation layers in magnonic spintronic devices.

5. Optics

In the last twenty years, the field of optics has seen a steadily increasing interest in hybrid materials. One reason behind this push towards the study of organic/inorganic hybrids, especially in optoelectronics, is related to the unique properties that allow to build innovative architectures that can bridge the gap between inorganic-based and polymer-based devices. Another advantage of this class of materials is related to the possibility of tuning their properties (like absorption, emission, refractive index) by changing some of the many parameters that regulate the mixture of organic and inorganic parts. However, combining organic and inorganic materials, which are in majority of the cases not compatible, is a challenge that is anything else but easy. For this reason, the study of new alternative fabrication strategies has become a pivotal point to permit the commercialization of some innovative ideas. Among all the possible methodologies, vapor phase techniques are quickly becoming very popular thanks to their limited production costs and high yields.

5.1. Photoluminescence

A combination of ALD and MLD can be used to produce multi-layered structures where organic and inorganic thin films are alternated and the resulting stack macroscopically behaves as a hybrid material. An example was shown by A. Tanskanen et al, where the authors developed a superlattice of ε phase Fe$_2$O$_3$ and monomolecular benzene layers deposited by ALD of iron oxide and MLD of iron terephthalate, respectively [54]. They experimentally demonstrated that in systems in which the iron oxide thin film thickness is reduced to values below 2 nm, the indirect optical bandgap ($E_g$) of the device suffers a blue shift from 2.0 eV of ε-Fe$_2$O$_3$ up to 2.3 eV, depending on the periodicity. The reduced dimension of the iron oxide films triggered these optical shifts of the $E_g$, which appear to be related to a quantum confinement in the oxide layer, but the authors also reported that further research on ultrathin ALD-grown ε-Fe$_2$O$_3$ is needed and envisioned.

In addition to the atomic or molecular precision that distinguishes the ALD/MLD methodology for hybrid device fabrication, this technique owns further, very unique characteristics. Thanks to the self-limiting growth mechanism which provides deposition of one atomic or molecular layer at the time, this technique allows to construct hybrid materials with molecular assemblies that cannot be obtained by other synthetic schemes. One intriguing example is the first reported ALD/MLD synthesis of a lanthanide-based NIR-to-Vis upconverter, reported by Giedraiityte et al [55]. In the field of medical diagnosis and bioimaging, the use of upconverters instead of traditional photoluminescent markers is an appealing solution, because it enables operation in the transparency window of tissues, avoiding autofluorescence. Many hybrid molecular complexes also offer greater sensitivity because they can come into closer contact with biological components than inorganic nanocrystals. In this paper it is shown that
a photoluminescent amorphous (Y,Yb,Er)-pyrazine thin film can efficiently upconvert three and two photons from NIR to Vis. The authors propose a mechanism of the excitation transfer, in which the cation Yb$^{3+}$ (and likely also the pyrazine complex) act as a sensitizer absorbing and re-emitting the incident radiation at energies that are compatible with the radiative excitations of the cation Er$^{3+}$ (figure 11(c)).

The photoluminescent films deposited on silicon have been characterized by NIR spectroscopy with an excitation radiation at 947 nm, showing 2-photon up-conversion emissions in green and red due to $^{3}H_{11/2}, ^{3}S_{3/2} \rightarrow ^{4}I_{15/2}$ and $^{4}F_{9/2} \rightarrow ^{4}I_{15/2}$ transitions, respectively. It was also shown that the hybrid film shows a blue emission peak but with a much lower intensity, because it is related to the 3-photon up-conversion transition from $^{3}H_{9/2}$ to $^{4}I_{15/2}$ (figure 11(a)). A further result that consolidates the compatibility to biological environments is that the increase of the incident NIR radiation’s power favors the emission of low frequency radiation (red), which have a higher penetration depth into tissues than emissions at higher frequencies. It is reported that the red/green up-conversion emission intensity ratio grows from 0.43 at an incident power of 0.23 W up to a value of 0.90 at 0.79 W.

Apart from the controlled fabrication of multilayered structures and the bottom-up growth of hybrid thin films, another interesting aspect of an ALD-type of processing is that it enables the top-down modification of soft porous materials by vapor phase infiltration of inorganic species into polymeric matrices. An interesting example of photoluminescent materials is shown in a work of Akyildiz et al where they modified polyester fibers via sequential vapor infiltration (SVI) of trimethylaluminum (TMA) [56]. The photoluminescence of polymers under UV irradiation is a phenomenon generally related to the presence of $\pi$-electrons and is commonly studied as it relates to the degradation of the polymer. In the case of polyester, it was found that the two emission bands of the pristine polymer can be red shifted by infiltration of Al$_2$O$_3$. The authors relate this behavior to the crosslinking between different polyester fibers upon formation of Al$_2$O$_3$ bridges. UV–vis spectroscopic absorbance and photoluminescence (PL) excitation spectroscopy showed a strong widening of the absorption band at 375–475 nm. These optical changes were characterized by measuring the absorption and PL internal quantum efficiency (IQE) under UV irradiation at 355 nm. The authors found that pristine PET fibers absorb 70% of the incident UV light with an IQE of 1.8%, meaning that the majority of the photogenerated charge carriers recombine in a non-radiative way, while after 90 SVI cycles at 90 °C the absorption of the hybrid PET-Al$_2$O$_3$ rises to 90% with an IQE of 25%. This significant increase of the IQE after SVI processing suggests that the presence of Al$_2$O$_3$ links between the polymeric chains modifies the electronic band structure, providing a more efficient radiative pathway. Apart from showing that photoluminescent materials can be obtained by a simplistic vapor modification of a commercial and inexpensive product, the authors proposed another interesting application. They demonstrate that, in agreement with literature, the PL performance of this semiconducting hybrid is related to its photocatalytic activity. The reason is that the radiative decay of the hybrid material is slower than the non-radiative recombination pathway of the pristine PET fibers and thus the carriers generated in the hybrid material have a longer lifetime, which would be beneficial for photocatalysis. Exploring this new property of the SVI-processed sample, they demonstrated the possibility of depositing Au and Ag nanoparticles on the surface of the PET-Al$_2$O$_3$ fibers by means of UV-photoreduction of metal ions, which by using light masking and laser rastering even allows patterning.

The top-down modification of high surface-area materials appears favorable for producing photocatalytic devices because porous materials are commonly easy to infiltrate with gaseous precursors. In a similar way to the before mentioned, Räupke et al performed infiltration of tris(8-hydroxyquinolinato) aluminum (Alq$_3$) by MLD into a commercially available silica aerogel with a pore size of 20 nm using trimethyl aluminum (TMA) and hydroxyquinoline (8-HQ) as precursors [57]. The authors also compared the effect of the presence of amine and hydroxyl surface groups on the formation of Alq$_3$. They demonstrated that dative bonding of TMA to an amine instead of a hydroxyl avoids the undesired hydrolysis of Alq$_3$ to Al$_2$OH and in this way preserves the high PL of Alq$_3$. After optimizing the PL of the deposited Alq$_3$, the authors demonstrated the application potential, using this process to coat and infiltrate high surface area silica aerogels, thereby showing that the ALD type of growth does not show the otherwise typical experimental limits of thermal evaporation such as shadowing. From an estimation of the penetration depth of the MLD deposition (tens of nanometers) the ability of this technique to produce high surface area photocatalytic materials appears clear. In view of these applications, the authors finally introduced a slight variation into the MLD recipe in which the first layer of Al$_2$O$_3$ is substituted by TiO$_2$, which has an electronic structure more suitable for photocatalysis. They found that in presence of TiO$_2$, the Alq$_3$ emission is strongly quenched because the photogenerated excitons in the Alq$_3$ layer are split and electrons are transferred to the conduction band of TiO$_2$, becoming available for catalytic reactions. In spite of this interesting novel approach in the field of MLD, it is worth mentioning that the attention on the MLD growth of luminescent quinolinates was driven by pioneering studies of Nilsen’s group [58].

### 5.2. Photonics and antireflective coatings

VPI of organic nanostructured templates has also been reported as an interesting strategy for the fabrication of inorganic three-dimensional nanomaterials with structures that would otherwise be difficult to produce. It is important to emphasize that, following this procedure, the construction of a hybrid composite is only an intermediate stage of the fabrication and the final device is purely inorganic. The organic three-dimensional structure acts as a mold for the inorganic material processed by vapor phase and is later removed. This, as demonstrated by Marichy et al, is a very interesting strategy for the fabrication of photonic crystals with complex designs. The authors construct a three-dimensional polycarbonate (PC)
template using direct laser writing (DLW) and infiltrate it up to saturation with TiO$_2$ using ALD [59]. In this way, once the polymer is calcined and removed, they are able to obtain a precise inverted copy of the PC template.

Apart from photonic crystals, other industrially appealing optical systems for light manipulation include antireflective (AR) coatings. Broadband AR coatings typically comprise multi-layered structures in which high and low refractive index films are alternated. In this field there is an increasing interest for polymer-based materials because of their easier applicability to polymeric substrates on which inorganic structures would typically delaminate. However, while the adhesion of an organic film is stronger, polymers have a narrow range of refractive indices, whereas AR coatings demand a strong refractive index contrast. To meet this requirement, Singaravelu et al proposed an AR coating compatible with PC substrates, which can be efficiently deposited by resonant infrared MAPLE [60]. The optimized AR coating is based on alternating films of TiO$_2$/poly(methylmetcrylate) (PMMA) and PMMA and yielded antireflective PC with a high transmission (97%) and a reflection coefficient in the visible range down to 0.5%.

5.3. Photovoltaics

Hybrid materials may also be excellent candidates also for photovoltaics (PV). Various examples of hybrid materials have been studied in the last 30 years in view of such applications. Among them Graetzel cells, also known as dye-sensitized solar cells DSSCs, are one interesting example on how organic dyes can operate in synergy with an inorganic matrix to produce a photocurrent. Even though DSSCs are still under extensive study [61], perovskites became recently more popular for PV and among those a relatively new and attractive class of hybrid materials evolved, hybrid perovskites. Since the first hybrid perovskite solar cell (PSC) was synthetized in 2009, this class of PV has seen a rapid evolution. In 2019 such hybrid materials have enabled fabrication of devices with a power conversion efficiency of almost 25% [62]. The main limiting issues for the commercialization of Perovskite solar cells include the lack of deposition methods for homogeneous thin films on a large scale, the rather poor stability of the materials and, in some cases, their toxicity. To address the first issue, the recent years have seen several proposals for growth, alternative to standard wet-chemical processing.
In 2013, Chen et al reported a clever methodology, called vapor assisted solution process (VASP), which allows to obtain organic/inorganic hybrid perovskite films of CH$_3$NH$_3$PbI$_3$ (MAPI), which bases on an in-situ reaction between a spin coated film of PbI$_2$ and vapors of CH$_3$NH$_3$I at 150 °C in N$_2$ atmosphere [63]. The authors showed that their procedure allows to grow a perovskite film of excellent quality, characterized by large grains and reduced grain boundaries. They fabricated a PV device with a 350 nm thick CH$_3$NH$_3$PbI$_3$ perovskite as active layer and characterized it by current density (J)–voltage (V) measurements under 100 mW cm$^{-2}$ simulated solar irradiation. The device exhibited a current density (J$_{sc}$) of 19.8 mA cm$^{-2}$, a fill factor (FF) of 66.3% and a power conversion efficiency (PCE) of 12.1%. The authors attributed these results to the high quality of the film produced by VASP.

Even though the approach, involving both liquid and gas phase, produces interesting results, as demonstrated with further and similar research lines [64], the wet-chemical processing step is still a factor that hinders upscaling. Two more recent papers show an approach towards production of perovskites solely relying on low-vacuum vapor phase techniques. One example is reported by Popov et al, where the authors demonstrate that the previously mentioned perovskite MAPI can be completely deposited by ALD [65]. The process consists of two steps. Initially, a thin film of lead iodide (PbI$_2$) is deposited from bis[bis-(trymethylsilyl)amide] Pb(btsa)$_2$ and tin(IV) iodide (SnI$_2$). Subsequently, the film is converted into MAPI by exposure of the ALD film to methyl ammonium iodide (MAI). Although it requires working in a rather narrow temperature range, this process allows a low deposition temperature and is therefore compatible with many substrates, even thermally sensitive polymers. Note that, even though the proposed process and the results obtained are very promising, the use of a Pb-based perovskite, being toxic and highly regulated, may not be an optimal solution and further research will be needed for finding alternative materials.

As an alternative to Pb-based PSCs, S. Sanders et al have shown that with a showerhead-based CVD reactor it becomes possible to grow methylammonium bismuth iodide (MBI) solar energy absorbing layers [66]. The reported stability of this hybrid material in atmospheric conditions, together with the upscalability of the process, make this solution very interesting, but the device still shows a low PCE. The authors state that improving the performance of such bismuth-based PSCs requires further solution and further research will be needed for finding alternative materials.

5.4. Plasmonics

Plasmonics is a further research field in which hybrid materials are explored and several examples of gas phase processes for creating hybrid plasmonic materials have been recently reported. The integration of organic constituents into plasmonic devices is a promising strategy to tune the properties of the plasmonically active materials without changing the geometry of the metallic nanostructures. In fact, once specific applications are envisioned, it is often required to tune the resonance frequency of the plasmon in order to match the requirements, which can be easily achieved by changing the surrounding media with polymers with different dielectric constants. In 2006, Takele et al reported an interesting study on hybrid nanocomposites in which silver nanoparticles were embedded into a polymeric matrix [68]. The hybrids were grown applying a vapor phase co-deposition of silver (as plasmonically active material) with various polymers including poly(hexano-6-lactam) (Nylon6), Teflon AF 1600 (TAF) or poly(methyl methacrylate) (PMMA). During the co-deposition, the dissolution probabilities of the Ag ions into the polymer also depended on the polymer itself, which lead to the formation of nanocomposites with different metal concentrations, spatial distributions and cluster sizes. After determining the metal content with EDX-SEM and characterizing the optical response of the various hybrids with UV–vis/NIR-spectroscopy, the authors studied the relation between the microstructure and the optical behaviour of the samples (PPR), highlighting the factors that affect position, intensity and broadening of the particle plasmon resonance for the various metal volume filling factors (f). They concluded that at low f (below 10%), the change of the dielectric constant of the surrounding is the main factor affecting the PPR. They measured a red shift of the plasmon resonance peak for the same Ag concentration when the dielectric constant of the matrix changed from 1.7 (in the case of Teflon/Ag) to 4.0 (in the case of Nylon-6/Ag). Once the metal concentrations rose higher than 10%, the larger particle sizes and the reduction of the interparticle distance became dominant over the red shift, finally causing a wide broadening of the plasmon resonance peak along with the metallic network being formed.

Since the birth of modern plasmonics at the end of the 1960s, one field in which plasmonic materials have shown great promise and performance is biotechnology. Here, the introduction of hybrid systems may be beneficial for increasing the biocompatibility and thus the sensitivity of the devices. For example, in order to serve as biosensor, the plasmon resonance needs to be compatible with the transparency window (650–900 nm) of a biological tissue. In 2002, Haes and Van Duyne reported that Ag nanotriangles, functionalized with self-assembled monolayers of covalently attached biotin molecules, were suitable to sense the protein Streptavidin down to concentrations of 1 pM [69]. A controlled assembly of hybrid materials has recently been used to demonstrate the sensitivity of devices. In a work by Maccaferrì et al, the gas phase deposition of organic molecules MLD has been proposed as a means to characterize the response of magnetoplasmonic nanoantennas, composed of an array of nickel nanodisks [70]. When characterizing a biosensor, one of the crucial parameters for defining the performance of a device is the surface sensitivity ($S_{surf}$), expressed as the shift of the localized plasmon resonance peak (Δλ*) divided by the change in thickness of the layer (Δt), of refractive index n, being sensed on top of the surface of the nanoantenna. In this particular
case, the magnetoplasmonic nanoantenna offers a unique sensing modality that permits enhancement of the surface sensitivity of a plasmon-based detector by triggering the magneto-optical activity of the ferromagnetic (FM) material with an external magnetic field. The sensing is based on the detection of the polarization changes $\Delta \lambda_\perp$, introduced by the change of the local refractive index due to the presence of a molecular film of thickness $t$ on the surface of the material. In order to be able to characterize such a sensitive detector, the choice of a technique able to produce $\Delta t$ with atomic precision is needed. As method-of-choice, MLD has been used to grow a polyamide-6.6 film on top of the nanoantenna. Being a polyamide, this polymer is representative for a broad variety of polymers/proteins and peptides and therefore is perfect for simulating a biological environment for which the nanoantenna opts. After performing polarization ellipticity measurements after each MLD cycle, the authors found a raw limit of detection of 0.5 nm and predicted that even discontinuous monolayers of PA-6.6 could be detected (figure 12(a)). The authors report that by performing the polarization measurement in reflection geometry, the calculated $S_{\text{surf}}$ is more than three times higher than the surface sensitivity of Au-based SPR detectors reported by 2015.

The sensitivity of the plasmon resonance to changes in the surrounding medium can be also used for innovative applications such as color filters and optical switches. Großmann et al realized a hybrid plasmonic optical switch fabricated by a thermally evaporated nanostructured thin gold film, coated with polystyrene (PS) that contained photochromic spiropyran molecules (SPO) [71]. This photochromic molecule undergoes a reversible ring-opening reaction when illuminated with UV light (at 365 nm) and was utilized in this work to alter the permittivity of the PS/SPO film (figure 12(b)). Using two-photon photoemission (2P-PEEM) the authors characterized the changes of the real part of the surface plasmon polariton wave vector $k_{\text{SPP}}(\omega)$, induced by the alteration of the dielectric environment. By exploiting the changes in the surface plasmon polariton (SPP) phase and the group propagation related to the changes in $k_{\text{SPP}}$, the authors could construct a switchable plasmonic lens. Finally, after reconstructing the SPP field amplitude from the 2P-PEEM data, they quantitatively characterized the optical changes of the plasmonic lens. The relative changes between the unswitched and switched states were about 5% and 18% in terms of focal length and depth of field, respectively (figure 12(c)). The authors stated that numerous parameters still need to be optimized in order to increase the performance of the lens. They also reported that the PS/SPO overlayer suffered rapid photodegradation that drastically reduced the $k_{\text{SPP}}$ delta between the two switching states. To address this issue, they proposed studies on different polymer mixtures and the use of different photochromic molecules such as azobenzenes.

5.5. Photoswitching

The application of azobenzenes is recently being studied by numerous research groups, because they show strong changes in their molecular dipole moment after photoswitching, but also because of their relatively high stability. In a recent paper of Khayyami and Karpipinen, the authors grew a superlattice (SL) of ZnO:Azobenzene and characterized its reversible photosensitive behavior [72]. They demonstrated that ALD/MLD allows to produce stable and homogeneous hybrids in which the functional photochromic molecules are integrated into an organic matrix in a highly controlled way. The ALD/MLD super-cycles lead to the formation of a superlattice that can be schematized as $[(\text{ZnO})_m+(\text{Zn}_2\text{O}_2\text{-C}_6\text{H}_4\text{-N = N-C}_2\text{H}_4\text{-C}_6\text{O}_2)_n+(\text{Zn-O})_m]$, where $m$ is the number of inorganic layers (equal to the number of cycles if within the ALD window and saturation regime) and $n$ is the number of monolayers contained in the superlattice (figure 13(a)).

The authors investigated the effect of trans-cis isomerization of the organic component of hybrid superlattices with different $m,n$ compositions upon irradiation with UV light, showing that the $\pi-\pi^*$ absorption band at 320 nm of the trans-isomer gradually decreases and shifts blue over time while the UV photoisomerization reaction takes place. The reversibility of the photoisomerization was verified by heating the samples at 100 °C for 24 h, but the intensity of the $\pi-\pi^*$ band of the trans-isomer was strongly reduced, showing that the photoisomerization was not quantitative (figure 13(b)). This observation was attributed to the evidence that SL structures affect the optical band gap and possibly increase the activation energy of the backward cis-to-trans reaction. Overall, the authors provided an interesting proof-of-concept of the ALD/MLD processed ZnO:azobenzene system for producing novel light-switchable devices.

The possibility of applications of photoswitchable materials are manifold, ranging from the modulation of biological processes to information and energy storage and new surprising applications have been proposed. Kettunen et al reported that nanocellulose aerogels coated with CVD TiO$_2$ show photoswitching behavior between water-repellent and water-superabsorbent states [73]. The first state of water repellence was induced by the presence of TiO$_2$ on the surface of the aerogel, while the second state, in which the material could absorb water to amounts of 16 times its own weight, was achieved after UV illumination at 350 nm. The water repellent state was recovered by storing the material in the dark, which required long time.

6. Bioapplications

Hybrid nanomaterials promise enhanced bioactivity resulting from the synergistic combination of both the organic and inorganic parts, therefore a series of recent studies involved research on organic-inorganic hybrid materials towards biomaterials sciences.

6.1. Bioactive hybrid materials synthesized by ALD/MLD techniques

Hybrid materials have been used for a wide range of biomedical applications, such as, tissue engineering, implant coatings with improved biocompatibility, antibacterial surfaces,
targeted drug delivery systems, biosensors etc. Hybridized organic-inorganic systems are very attractive biomaterials since they show enhanced physical or chemical properties compared with their individual counterparts, while minimizing many of their specific limitations.

Various vacuum-based deposition techniques were applied to design hybrid bioactive or bioinert surfaces. However, ALD/MLD techniques have not yet been extensively applied in that field. Among the scarce examples, a novel class of hybrid materials, containing essential amino acids combined with biocompatible titanium, called titinates, were obtained by Momtazi et al applying MLD [74]. The films were grown from titanium tetra-isopropoxide (TTIP), glycine and L-aspartic acid as precursors. L-Arginine has also been used, however, without success. The hybrid films based on TTIP and succinic acid were investigated and compared with their L-aspartic acid based counterparts due to their structural similarities. The growth dynamics were monitored in situ with a quartz crystal microbalance (QCM). FTIR and XPS analyses proved the hybrid nature of the grown materials and that the organic linkers preferably react with titanium through their carboxylate functionalities. The wettability of the hybrid films
with glycine and L-aspartic acid was investigated by measuring the contact angle of water. Ti-glycine and Ti-L-aspartic acid films showed hydrophilic nature with a contact angle of approximately 30° for films deposited at temperatures in the range of 225–350 °C. The contact angle for both hybrid films did not change significantly within this range of deposition temperatures. Both films were used as substrates for the growth of epithelial cells (rat goblet cells) and their proliferation has been monitored. The cell proliferation on these substrates was significantly increased compared to uncoated coverslips. It was shown that epithelial cells can be successfully grown on such amino acid-based surfaces and that the cells retain a high viability.

Tailoring the surface functionality of materials is an important task in tissue engineering, specifically for designing bioactive and biocompatible materials. In a follow-up work, Momtazi et al [75] explored the MLD technique for building surface coatings consisting of bioactive compounds: amino acids, nucleobases, and the biocompatible metal titanium. The substrates were coated using TTIP and L-lysine, glycine, L-aspartic acid, L-arginine, thymine, uracil, or adenine as building units. Subsequently, immunofluorescence, cell attachment, proliferation, and viability of rat conjunctival epithelial goblet cells, were analyzed. Using first-passage conjunctival goblet cells, the number of cells attached to the various MLD substrates was quantified after 3 h. The results showed that amino acid-, nucleobase-, and titanium oxide-coated substrates, prepared by MLD, do not reduce the cell attachment. Initial proliferation results indicated that proliferation of first-passage conjunctival goblet cells on Ti-L-lysine and TiO₂ was significantly higher than on uncoated coverslips. Cell growth studies on further substrates, containing different amino acids and nucleobases, were also performed. Figures 14(a) and (b) show that the amount of viable conjunctival goblet cells, grown on the MLD substrates Ti-glycine, Ti-L-aspartic acid, Ti-L-arginine, Ti-adenine, Ti-uracil, Ti-thymine, and TiO₂, was significantly higher than that on bare coverslips.

The viability of the cells was tested using the calcein acetoxymethyl/ethidium homodimer-1 live/dead assay. Figure 15(a) shows a selection of fluorescence micrographs of the cells grown on the various coated substrates. The staining demarks the live rat conjunctival goblet cells as green and the dead cells as red, while the merged images show both. The diagram in figure 15 shows the viability on (b) titanium-amino acid coated substrates and (c) titanium-nucleobase coated substrates. The results showed that the cell attachment on the MLD-coated substrates was at least as good as on coverslips. It was demonstrated that the MLD substrates increased the cell proliferation, except for MLD substrates containing terephthalic acid, which revealed a lower proliferation. Generally, the study showed that the cell viability was very high (>85%) for all substrates.

In a subsequent work, the same group [76] described in more detail the MLD-growth of organic-inorganic hybrid thin films by combining titanium tetra-isopropoxide (TTIP) and nucleobases, such as, thymine, uracil or adenine. QCM measurements proved that all systems exhibited the ALD-characteristic self-limiting growth. The bonding modes of the films have been characterized by FTIR, XPS and x-ray diffraction, confirming the hybrid nature of the as-deposited films. The wettability of the surfaces was investigated by measuring the contact angle of water on the various films. The films appeared to be highly hydrophilic with contact angle values of 19 ± 2° for Ti-thymine (deposited at 225 °C), 19 ± 1° for Ti-uracil (deposited at 225 °C), and 45 ± 3° for Ti-adenine (deposited at 250 °C). This hydrophilicity is an asset for cell growth. Also, the effect of water on the film thickness upon immersion was investigated. Most of the nucleobases leached out during the initial 15 min of immersion in water but thereafter the thicknesses remained nearly constant over time.

A series of recent studies has demonstrated that ALD/MLD can be used to fabricate biocompatible substrates via molecular design, which enables the use of MLD within the field of regenerative medicine and tissue engineering for regulating cell and tissue development. Such biomaterials can be applied for implants where the surface functionality is a key factor for adhesion and interaction of the implant with the surrounding tissue.

Even though the work is not involving hybrid materials but purely inorganic materials, it is worth mentioning that Putkonen et al [77] applied ALD to grow biocompatible hydroxyapatite thin films from Ca(thd)₂ (thd = 2,2,6,6-tetramethyl-3,5-heptanedionato) and (CH₃O)₃PO on Si (100) and Corning (0211) substrates. The importance of this process lies in the fact that such materials are very difficult to obtain from the gas phase and the proof of the growth by ALD allows for a precise tuning of the coating thickness, which is not possible in other ways. The biocompatibility of the substrates was demonstrated with cultures of Mouse MC 3T3-E1 cells. It was shown that, according to the bioactivity studies, the cell proliferation was enhanced on as-deposited ALD-grown Ca–P–O films and greatly enhanced on films annealed at 500 °C, in comparison with references grown on borosilicate glass or polystyrene, which are commonly used for cell cultures.

Puvvada et al [78] investigated the growth of E. coli bacteria on ALD-grown ZnO nanocoatings on cotton fabrics with systematic variations of thicknesses between 0.2 and 20 nm. Woven cotton fabrics were conformally coated with ZnO films using ALD at 90 °C. They examined the bacterial growth on both treated and untreated cotton fabrics, fully immersed in aqueous dispersions of E. coli as well as dry test conditions. In fully aqueous conditions, a monotonic increase in the number of bacteria was observed for cotton fabrics coated with 1, 3, and 10 cycles of ZnO ALD. The samples coated with 10 cycles showed a 5-fold increased bacterial growth compared to the positive control. Coatings with 50 cycles (approximately 10 nm) and beyond resulted in quantitative bacterial death. This may be related to the dissolution of ZnO. At low concentrations, the Zn²⁺ ions act as a nutrient, promoting bacterial growth. In contrast, high concentrations of Zn²⁺ are cytotoxic for E. coli. Similarly enhanced bacterial growth was observed
for up to 10 ALD cycles under pseudo-dry growth conditions. However, after 100 ALD cycles (∼20 nm) approximately 1 d was required to cause complete E. coli death.

The ability of ALD films to support cell attachment was also demonstrated by Liang et al [79] They grew ultrathin conformal alumina and titania films on highly porous poly(styrene-divinylbenzene) (PS-DVB) particles applying low-temperature ALD processes in a fluidized bed reactor. The biocompatibility of the resulting composites was tested by hydroxyapatite (HA) formation and cell adhesion. The ability of the uncoated and coated porous particles to promote cell attachment and spreading was tested using a model cell, NIH/3T3 fibroblasts. The bioactivity studies of the composite particles were performed in vitro by immersion of the substrates into simulated body fluid (SBF) for various periods of time. The improved bioactivity of the polymer substrates was demonstrated with the formation of HA on the surface of the substrates from a simulated body fluid. Indeed, an accelerated formation of HA on the ALD-modified polymer surface was observed, which was likely caused by the negatively charged surface provided by the ultrathin ceramic interface.

Panchawagh et al [80] studied a flip–chip-based encapsulation process using surface micromachined polysilicon caps for packaging of MEMS actuators for BioMEMS applications. Aimed at protecting the MEMS structures from particulate matter present in biological liquids, the device was coated with alumina by ALD. Afterwards the Al₂O₃ coating was terminated with a covalently bound hydrophobic monolayer using a tridecafluoro-1,1,2,2-tetrahydrooctylmethylbis-(dimethylamino) silane (FOMB(DMA)S, C₈F₁₃H₂(CH₂)₃Si(N(CH₃)₂)₂) precursor. Such coatings may find their use in biomedical microelectromechanical systems and ‘lab-on-a chip’ microfluidic devices, including in vivo pressure sensors, implantable biochemical sensors, DNA sequencing chips, drug delivery systems, micro-assays, micro-electrode arrays, microsurgical tools and sensors.

Controlled delivery of bioactive substances with local restriction is of interest in medicine and life sciences. Boehler et al [81] presented a new approach for the fabrication of a release system for bioactive substances which will combine efficient control over the release with an adequate storage capability. An SEM image showing the complete stack of layers after vapor phase polymerization (VPP) is provided in figure 16(a). They synthesized drug-loaded hybrid storage films, containing fluorescein as a model substance, by blending the molecule into PEG and subsequently converting the polymer into a solid hybrid material using an ALD process. They spin-coated a porous Si substrate with the drug-containing PEG film and subsequently hybridized it. Subsequent coating with conducting polymer layers by VPP completed the assembly. For the evaluation of the biocompatibility of the system, in vitro tests were performed by culturing the neuron like cell line SH-SY5Y on top of the sample. After incubation for 24 h, the cells were fixed and imaged by fluorescence microscopy (figure 16(b)) and SEM (figure 16(c)).

The pictures show homogeneously spread cells growing on the surface of the material. The cells formed a network, thereby clearly demonstrating that the surface was suitable as a substrate for cell culturing.

In a very interesting approach, Folestad and coworkers performed ALD on pharmaceutical particles for controllable drug delivery in a fluidized bed reactor, which allows coating of particles. This work showed the first dry state surface modification of pharmaceutics with complete and conformal coating of particles. The results showed how single particle and bulk properties, such as dissolution rates, dispersibility and heat transfer, can be effectively modified and tailored with as few as 2–4 ALD cycles. The dissolution rates were reduced.
for budesonide and lactose particles with increasing alumina film thickness, confirming the potential of this technology for controlling the drug release [82].

The same group further demonstrated the successful nanoengineering of crystalline and amorphous surfaces of micro sized lactose particles of two sizes (d50 = 3.5 and 21 μm), contrasting TMA/ozone to TMA/water deposition processes [83]. Their properties, including dissolution and dispersibility, were tailored for drug delivery applications. The deposition process was carried out at ambient conditions in a fluidized bed reactor with low numbers of cycles (4 to 14). An improved dissolution and an extended release were achieved by the nanoengineering of both crystalline and amorphous surfaces, showing that this novel concept opens up exciting opportunities for applications in the pharmaceutical, medical, biological, and advanced materials fields.

6.2. Bioactive hybrid materials synthesized by CVD

The design of gas-phase grown organic-inorganic hybrid materials suitable for biomedical applications is relatively unexplored and allows plenty room for novel developments and studies. Given the plethora of compositional and structural possibilities, considerable research is necessary on both short- and long-term to better understand how the coating will behave in an active biological environment. However, some initial experiments already showed promising results, giving rise to an optimistic view on novel developments in forthcoming years.

Several types of CVD processes were applied to obtain organic-inorganic hybrid materials for biomedical applications. Using pulsed-PECVD, Lewis et al [84] demonstrated conformal coatings of hexamethyldisiloxane (D3) on nonplanar substrates that are suitable for implantation, including copper wires and neural probes, for application as insulating biomaterials. They showed that the obtained coatings were resistant to prolonged immersion in warm saline solution, and that the wire coatings produced by pulsed PECVD showed higher flexibility than the analogous coatings deposited by continuous-wave (CW) excitation.

With the aim to develop an insulating thin film biomaterial, O’Shaughnessy et al [85] studied the iCVD-induced polymerization of trivinylmethyldisiloxane (V3D3). The polymerization was initiated by tert-butylperoxide (TBP). The results showed that the trifunctional nature of the V3D3 monomer undergoes self-polymerization. In a follow-up, the same authors evaluated the biocompatibility and long-term stability of the deposited poly(1,3,5-trivinylmethyldisiloxane), poly(V3D3) [86]. The results of the biocompatibility studies with PC12 neuronal cells demonstrated that this polymer is not cytotoxic and does not influence the cell proliferation. They also showed that poly(V3D3) is insoluble in both polar and nonpolar solvents and that its adhesive strength to silicon substrates is very high. Consequently, poly(V3D3) shows promise and for a potential use as permanently implantable insulating thin film.

6.3. Bioactive hybrid materials synthesized by MAPLE technique

The so-called MAPLE technique has also been applied to fabricate hybrid coatings for biomedical applications. Bigi et al [87] investigated the deposition of thin films of HA nanocrystals with a varying alendronate content on titanium substrates in order to combine the bioactivity of HA with the local availability of alendronate. The results showed that the coatings had an enhanced bioactivity and were able to promote osteoblast differentiation and to inhibit osteoclast proliferation. The importance of the results lies in the finding that the MAPLE-synthesized coatings are suitable to promote bone formation and prevent bone resorption.

In another approach with the same technique Ciobanu et al [88] studied the physico-chemical and biological properties of polymer nanocomposite thin films containing iron oxide nanoparticles in a dextran matrix. The demonstrated good viability of HepG2 cells grown on dextran-coated magnetite thin films, which exhibited a normal actin cytoskeleton, suggesting that these cells underwent normal cell cycle progression. The testing confirmed that hybrid iron oxide-dextran...
nanocomposites could be possibly used as a potential marker for biomedical applications.

Paun et al. [89] reported on MAPLE of composite biocompatible antibacterial coatings consisting of silver nanoparticles combined with polymer blends (polyethylene glycol/poly(lactide-co-glycolide), PEG/PLGA blends). The initial investigations confirmed the expected antibacterial properties of the coatings, which was demonstrated with E. coli.

Hybrid nanostructures, consisting of HA and sodium maleate-vinyl acetate copolymer (MP), deposited by MAPLE on Ti, have been demonstrated by Sima et al. [90]. In this work, specific biological qualities required in bone implantology were investigated. The in-vitro studies demonstrated that human primary osteoblasts (OBs) firmly adhered to Ti coated with HA–MP as indicated by the cytoskeleton and vinculin dynamics. OBs spread on the biomaterial surface and formed groups of cells which during their biosynthetic activity expressed OB phenotype specific markers (collagen and non-collagenous proteins) and underwent controlled proliferation. The results indicate that the HA–MP coating is a structure, which is well tolerated by the bone cells.

7. Further applications

7.1. Hybrid diffusion barriers

The coating techniques ALD/MLD and CVD also found their application for fabrication of permeation barriers against water vapor. In order to be efficient, a high activation energy for the permeation and a sufficiently high flexibility of the coating is needed to obtain an ultralow water vapor transmission rate (WVTR). A review of the recent literature shows that flexible hybrid gas permeation barriers were grown by ALD/MLD using a large variety of organic and inorganic precursors. Zhang et al. [91] studied Al₂O₃/ZrO₂/alucone hybrid nanolaminates for an encapsulation of organic light-emitting diodes (OLEDs). The WVTR of the nanolaminates was measured with Ca tests. The experiments showed that the moisture barrier performance was improved with increasing the number of dyads (Al₂O₃/ZrO₂/alucone) and the best obtained WVTR reached 8.5 × 10⁻⁵ g m⁻² d⁻¹ at 25 °C and a relative humidity (RH) of 85%. In a practical test, Zhang et al. [91] measured the lifetime of OLEDs after encapsulation with ALD. The half lifetime of a green OLED with the initial luminance of 1500 cd m⁻² reached 350 h using three stacks of Al₂O₃ (15 nm)/ZrO₂ (15 nm)/alucone (80 nm) for encapsulation.

Jang et al. [92] reported on plasma enhanced ALD (PEALD) based Al₂O₃/organic inorganic nanohybrid gas barrier films, which exhibit ultralow water vapor transmission rate (WVTR), high activation energy for permeation, high optical transmission in visible light, and a sufficient flexibility. The WVTR of the barrier reached 7.83 × 10⁻⁵ g m⁻² d⁻¹ and was measured at a temperature of 60 °C and 90% relative humidity. Furthermore, the value of the activation energy for the gas permeation was as high as 103.10 kJ mol⁻¹.

Bülow et al. [93] grew multilayers of aluminum oxide (Al₂O₃) and benzene-based polymer on polyethylene naphthalate (PEN) substrates by PEALD and PECVD at 80 °C in the same reactor. Triethylaluminium (TMA) and oxygen plasma were used as precursors for an Al₂O₃ growth by PEALD, while benzene served as precursor for the deposition of the polymer by PECVD. The resulting hybrid structure allowed decoupling of the defects between the
individual Al$_2$O$_3$ layers and created more tortuous paths for the water molecule permeation. A WVTR value of $1.2 \times 10^{-4}$ g·m$^{-2}$·d$^{-1}$ was measured at 60 °C and 90% relative humidity for a multilayer with 3.5 dyads of 25 nm Al$_2$O$_3$ and 125 nm benzene polymer. In addition, the authors reported that single Al$_2$O$_3$ films grown by PEALD show a significantly better barrier performance than thermally grown layers.

The combination of alucone (MLD) and Al$_2$O$_3$ (ALD) nanolaminate films for thin film encapsulation (TFE) at low temperatures has been evaluated by Xiao et al [94]. The study revealed that the encapsulation layers grown with O$_3$ as counter precursor were smoother than those grown with H$_2$O, even if obtained under identical processing conditions. The WVTR measurements showed significantly better results for the O$_3$-based laminates with the values decreasing linearly from $3.22 \times 10^{-3}$ g·m$^{-2}$·d$^{-1}$ to $2.37 \times 10^{-3}$ g·m$^{-2}$·d$^{-1}$ as the number of laminate layers increased from one to three. The corresponding trend for the H$_2$O-based laminate was from $1.83 \times 10^{-3}$ g·m$^{-2}$·d$^{-1}$ to $5.92 \times 10^{-4}$ g·m$^{-2}$·d$^{-1}$. Obviously, the use of O$_3$ instead of H$_2$O as the oxygen source improved the barrier properties of the hybrid nanolaminate. The authors further applied these hybrid encapsulation films to OLED devices. The results showed that the lifetime of OLEDs with O$_3$-based encapsulation was approximately two-fold longer than the H$_2$O-based encapsulation. Thus, not only the material selection for a hybrid alucone/Al$_2$O$_3$ encapsulation, but also the selection of the source chemicals appears to play a critical role for the efficiency of the resulting laminate. In a following study, the same group [95] compared the WVTR values and surface roughnesses of inorganic Al$_2$O$_3$ films and Al$_2$O$_3$/alucone hybrid films. The samples with an Al$_2$O$_3$ layer of 50 nm thickness, deposited by ALD at 80 °C, showed higher surface roughness (0.503 ± 0.011 nm), higher WVTR (3.77 × 10$^{-4}$ g·m$^{-2}$·d$^{-1}$), and lower transmittance values (61%) when compared with the Al$_2$O$_3$/alucone hybrid nanolaminates, fabricated under the same conditions. A bending test, applied to single Al$_2$O$_3$ layers, demonstrated an increased WVTR upon bending, while the film with a 4 nm alucone layer, sandwiched between Al$_2$O$_3$ layers, showed lower surface roughness, better barrier performance (WVTR = 9.94 × 10$^{-5}$ g·m$^{-2}$·d$^{-1}$), and higher flexibility and transmittance.

Jen et al [96] also studied Al$_2$O$_3$/alucone nanolaminate films grown by varying the ratio of ALD:MLD cycles. The laminates were deposited at 135 °C on Kapton substrates using TMA and H$_2$O for ALD of Al$_2$O$_3$ and alternating TMA/Ethylene glycol exposures for the MLD of alucone. The authors also pointed out that the hybrid Al$_2$O$_3$/alucone nanolaminate films exhibit better diffusion barrier properties and flexibility than pure Al$_2$O$_3$. The critical tensile strains (CTSSs) and WVTR values were measured for the nanolaminate samples with cycle ratios ranging from 1:1 to 6:1. The highest CTS, obtained from 1:1 and 3:1 nanolaminate films, were ~0.90% and ~0.98%, respectively. These values are much higher than those of pure alucone or Al$_2$O$_3$ films, which are in the range of 0.5-0.6%. Apparently, the higher CTS for the nanolaminates result from better cross-linking of the organic constituent than it is the case in the MLD alucone. The WVTRs tests for the different nanolaminate films at 38 °C, 85% RH, showed that the 1:1 nanolaminate yielded the highest WVTR of ~1 g·m$^{-2}$·d$^{-1}$, similar to the uncoated Kapton substrate. The WVTR of the nanolaminate films could be dramatically improved by increasing the Al$_2$O$_3$ volume fraction within the nanolaminate, which was attributed to a higher density of the material and the mentioned increased cross-linking within the nanolaminate films.

For enhancing the moisture barrier properties of polydimethylsiloxane (PDMS) films, Choo et al [97] proposed filling the PDMS free volume with aluminum oxide (Al$_2$O$_3$) by ALD. Three types of thin films were grown on Ca: (a) Al$_2$O$_3$, (b) Al$_2$O$_3$/PDMS, and (c) PDMS/Al$_2$O$_3$. The WVTR values of the PDMS/Al$_2$O$_3$ and Al$_2$O$_3$/PDMS films, measured at 45 °C and 65% RH, were 5.1 × 10$^{-3}$ g·m$^{-2}$·d$^{-1}$ and 1.46 × 10$^{-3}$ g·m$^{-2}$·d$^{-1}$, respectively. The WVTR value was lower when Al$_2$O$_3$ was deposited on the PDMS layer. The apparent reason for this enhancement is the filling of the free volume in the PDMS with Al$_2$O$_3$. For the Si/Al$_2$O$_3$/PDMS sample EDS mapping showed a clear interface between the Al$_2$O$_3$ and the PDMS layer, while the Si/PDMS/Al$_2$O$_3$ sample showed a diffusion of Al into the PDMS.

72. Wettability–filtration–sorption

The ability to adjust and control wettability, surface reactivity, and surface energy of materials and natural polymers is important for a broad range of applications.

Hydrophilic cellulosic cotton fibers were turned hydrophobic with a low number of ALD Al$_2$O$_3$ cycles in a work by Hyde et al [98]. Oldham et al [99] deposited three layers consisting of ZnO/alucone/Al$_2$O$_3$ on electrospun nylon nanofibers for a use in filtration and product separation. They demonstrated that coating with TMA/H$_2$O or DEZ (diethylzinc)/H$_2$O enhances the surface wetting due to the higher hydrophilicity of the inorganic oxide relative to the polymer. They also showed that there is a dependency of the wetting properties on the extent of precursor penetration into the polymer bulk. At lower deposition temperatures, where the precursor penetration is more impeded, the surface appears more hydrophobic than the starting material, whereas at higher processing temperatures or for higher numbers of cycles, the resulting material is more hydrophilic.

Gong et al [100] reported the modification of the wetting properties of PDMS by creating a hybrid oxide/polymer buffer layer using a VPI (SVI) process, ALD-Al$_2$O$_3$ and MLDAlucone coatings. The water contact angle of the sample was monitored over time to assess the temporal stability of the surface. It was shown that the PDMS surface became hydrophilic after TMA/water infiltration and 100 cycles of alumina ALD deposited at 120 °C. After 48 h exposure to lab air, the surface became more hydrophobic and the water contact angle increased from ~20° to ~65°. The same type of substrates (TMA infiltration + ALD-Al$_2$O$_3$) were also synthesized at 60 °C and left inside the reactor at the same temperature under Ar purge for 48 h with a similar result. When the sample was
measured immediately, the ALD modified surface was hydrophilic and the contact angle increased over time after exposure to air.

Saric et al. [101] presented an approach towards controlled modification of metal-oxide surfaces with organic molecules, which resulted in the creation of hybrid materials.

They reported on a pulsed vapor phase copper-free azide—alkyne click reaction of organics on ZnO using the ALD processing setup. The process involves an in-situ two-step reaction consisting of sequential exposures of ZnO to propionic acid and benzyl azide.

Ambrožič et al. [102] reported the first catalyst-free formation of organosilica hybrid nanohemispheres with terminal mercaptopropyl functional groups, grown on ALD-deposited Al2O3 thin films. The nanohemispheres were synthesized via cooperative condensation/hydrolysis and thiol-ene reactions of heterobifunctional silanes. The process is based on a two-step approach consisting of an initial silanization of a 50 nm thick ALD-deposited Al2O3 film with vinyltrimethoxysilane (VTMS), followed by a photo-promoted thiol-ene click reaction with (3-mercaptopropyl)trimethoxysilane (MPTMS). The surface-chemical properties and wetting behavior of the obtained hybrid films were investigated. Figure 17(c) shows that after treatment with VTMS, the alumina surface becomes significantly more hydrophobic, exhibiting a contact angle of 84°, which is due to the terminal vinyl groups. After the two step silanization process the hybrid is more hydrophilic (contact angle 62°) than the VTMS-modified alumina due to the larger number of −OH groups originating from the bound silanol species (figure 17(d)).

The fabricated materials offer a great potential for the development of hierarchically structured silanized thin-films for bioimaging and biosensing of thiol-carrying biomolecules through the formation of disulfide bridges.

McGuinness et al. [103] established a new, scalable, solvent-free, post synthesis treatment for transforming nanoporous polymers into novel hybrid membranes with increased stability, that have the potential to supplant energy-intensive distillation processes for separation of organic solvents. They applied VPI of polymers with an intrinsic microporosity 1 (PIM-1) hollow fiber membranes with several different metal-organic precursors, including TMA, DEZ, or TiCl4 and water vapor, creating an intertwined metal oxide network. SEM/EDX, TEM and XRD analyses confirmed that the amorphous metal oxide is homogeneously distributed throughout the polymer bulk. The authors studied the effects of VPI-processing conditions on the metal oxide loading, microporosity and chemical stability in organic solvents. The amount of metal oxide loading is quantified with thermogravimetric analysis (TGA), and the microporosity of the hybrid membranes was measured via N2 physisorption. The results from PIM-1 hollow fiber membranes, infiltrated with three different metal-organic precursors, TMA, DEZ, and TiCl4, are presented in figure 18. These data show that the VPI chemistry and processing conditions affect the amount of metal oxide loading and therefore, the loading within a PIM-1 membrane can be controlled by the membrane’s skin layer thickness, the precursor exposure time, pretreatment, precursor chemistry, VPI process temperature, and the number of VPI cycles. Figure 18(a) shows that the Al2O3/PIM-1 hybrid membrane shows significantly higher metal oxide loading than the other chemistries, yet it exhibits the nearly identical internal surface area, with only an 18% drop in surface area compared to pristine PIM-1. Longer VPI exposure times or more VPI cycles increase the metal oxide loading, enhance the metal oxide penetration, and decrease the Brunauer−Emmett−Teller (BET) surface area (figures 18(b), (c)). The obtained hybrid membranes show significant improvements in the chemical stability as compared to the initial polymer. They were tested against various solvents that dissolve PIM-1: tetrahydrofuran (THF), dichloromethane (DCM), and chloroform (CHCl3). All of those solvents dissolve PIM-1 within minutes, while all hybrid membranes remained stable throughout 3 months. It was shown that the Al2O3/PIM-1 membranes exhibited higher stability for dissolution in comparison to the hybrid membranes infiltrated with ZnO and TiO2 chemistries. As an example, figure 18(d) illustrates the long-term stability of Al2O3/PIM-1 membrane in THF. While PIM-1 membranes fully dissolve within minutes, Al2O3/PIM-1 hybrid membranes lose only 10% of their weight after 1 month of immersion.

The hybrid membranes could be applied for separations in aqueous media, since they show a change in hydrophilicity, as proven by both water sorption experiments and water contact angle measurements.

The organic solvent nanofiltration (OSN) and organic solvent reverse osmosis (OSRO) performances of these hybrid Al2O3/PIM-1 thin-film composite membranes were also tested in a continuous cross-flow filtration system with ethanol, n-heptane, toluene, and tetrahydrofuran as solvents. The results show that in contrast to the pure polymeric PIM-1 membranes, hybrid Al2O3/PIM-1 membranes show consistent (more than 95%) polystyrene dimer rejection in all four solvents. The membranes not only outperform untreated PIM-1 membranes for chemical separations in standard environments, but also provide consistent performance in environments which would otherwise swell or even completely dissolve the pristine polymer. The authors revealed that with this added chemical stability, the obtained hybrid membranes can even be applied for reverse osmosis in organic solvent, which is difficult to realize using pristine PIM-1.

Barry et al. [104] provided analysis of SIS-treated porous polymeric foams based on polyurethane and polyimide using alternating exposures to an organometallic precursor (DEZ or TMA) and deionized H2O. Initially, the TMA/polyurethane interaction was studied during individual TMA and H2O exposures for Al2O3 ALD SIS at 80 °C, but ZnO SIS was also studied. From the FTIR spectral analysis the authors concluded, that compared to the TMA, the spectral changes for DEZ-exposed polyurethane foams were 5–7 times smaller, indicating either a lower reaction rate or a smaller density of the reactive sites for DEZ on PU. The efficacy of SIS processing to functionalize polymeric foams with subsequent binding of superoleophilic compounds were also explored. The foams were functionalized using two different silane agents: (g-aminopropyl) triethoxysilane.
(APTS) and butyldimethyl(dimethylamino)silane (BDMS) by SIS. The results of sorption capacities are presented for both untreated and functionalized polyurethane foams. A relatively low sorption, without any selectivity for both water and oil, was observed for untreated polyurethane foams. The authors demonstrated that the surface functionalization dramatically affected both selectivity, the total amount adsorbed, and the kinetics. For example, untreated foams needed minutes to reach their maximum crude oil sorption capacity of \( \sim 7 \text{ g g}^{-1} \), while the treated foams reached \( \sim 30 \text{ g g}^{-1} \) in seconds.

SIS treatment of two types of open cell foams, polyurethane and polyimide, through alternating exposures to vapors of TMA and deionized H\(_2\)O, was demonstrated by Barry et al [105]. In the following report Waldman et al [106] extended the library of SIS-modified polymer nanocomposites to the
treated cotton is first ‘presoaked’ with water. This performance loss in the sorption capacity was observed, even if the ALD-buoyant on the water’s surface and continuously sorb oil. No but does not substantially sorb water, allowing it to remain untreated cotton’s selectivity for water sorption over oil sorption. In contrast, the treated cotton sinks through the oil layer previously undescribed polymer system and a new application space, polyethersulfone (PES) ultrafiltration membranes.

Short et al [107] demonstrated a vapor-phase modification approach to create a new class of oil sorbents composed of cellulose materials (cotton) coated with a subnanometer layer of an inorganic oxide. they showed that one to two ALD cycles are sufficient to drive this transformation and create a hydrophobic material that preferentially absorbs oil over water. Compared to untreated cotton this new cellulose sorbent remains buoyant in water indefinitely and achieves a selective oil sorption capacity of 23 g g$^{-1}$ or 1.05 g cm$^{-3}$, which is at least 35 times better than untreated cellulose in simulated conditions of oil dispersed in water with wave agitation. While untreated cotton is a good nonselective sorbent for oil, readily absorbing water, the ALD-treated cotton sorbents showed the opposite selectivity for oil sorption in mixed oil and water conditions. Figure 19 demonstrates this preference in a series of photographs where the sorbent materials are immersed into an oil–water mixture.

Untreated cotton quickly sinks through the top oil layer. Once in contact with water, the untreated cotton preferentially sorbs the water, increasing its density and eventually leading to its sinking. Once fully immersed in water, droplets of previously sorbed oil begin to visibly desorb, indicating the untreated cotton’s selectivity for water sorption over oil sorption. In contrast, the treated cotton sinks through the oil layer but does not substantially sorb water, allowing it to remain buoyant on the water’s surface and continuously sorb oil. No loss in the sorption capacity was observed, even if the ALD-treated cotton is first ‘presoaked’ with water. This performance, the simplicity of the synthesis and potential for retained biodegradability, makes these materials exciting for oil spill remediation in marine environments.

Cellulose nanofibril (CNF) nanopaper modification, applying just a few cycles of metal oxide ALD to modify the surface chemistry, wetting properties, and strength upon wetting, were presented by Li et al [108]. Water contact angle measurements confirmed that the ALD process modifies the nanopaper’s surface chemistry, showing a significant increase in the water contact angle upon 1 ALD cycle of either Al$_2$O$_3$ or TiO$_2$. Water completely wets the untreated nanopaper, while after modification with 1 or more ALD cycles of Al$_2$O$_3$ or TiO$_2$ water droplets ‘bead up’ showing a contact angle $\geq$80°. Applying more ALD cycles, this contact angle can be further increased to as much as 115°. The authors revealed that the increase of the hydrophobicity of the ALD modified CNF nanopaper is probably due to an increase of the concentration of hydrocarbons at the nanopaper’s surface.

It was demonstrated, that ALD-treated nanopapers with both TMA–H$_2$O and TiCl$_4$–H$_2$O chemistries show an increased wet strength under aggressive sonicating conditions. In contrast to the above, the untreated nanopaper was completely broken apart and dispersed in water immediately. The concentration of dispersed CNF in water over the sonication time for different ALD treatments was measured with optical transmission spectra. In addition, the authors also investigated the factors that may cause this increase in the wet strength, enhanced hydrophobic attractions or stronger hydrogen bonding between the CNF fibers. From DFT calculations the authors concluded that surface terminations with M–OH on the cellulose CNF, created by the metal oxide, likely increase the hydrogen bond strength between the fibers and impede CNF hydration and dispersion. The performance of the ALD-treated nanopapers for preferential transport of n-hexane over water was also investigated. The results showed that they are promising membranes, suggesting their potential for use in oil/water demulsification devices.

7.3. Metal-organic frameworks from the gas phase

Metal-organic frameworks (MOF) are highly ordered hybrids structures, consisting of inorganic atoms connected via organic linkers with a large free inner volume. Due to their porous structure, MOFs have an ultra-high surface area, which can be functionalized by gas-phase methods. Thanks to their unique properties, they are considered for numerous applications including catalysis, gas storage, molecular separations, mechanical sensing, as low-$k$ dielectrics, and for ion conductivity [109]. Thus far, almost all experimental routes for MOF preparation involve wet chemical coupling of metal salts and organic linkers and often require solvothermal conditions. Only recently first gas-phase synthesis approaches for MOF fabrication were demonstrated and the focus of these studies lies mostly in the proof-of-concept and expanding the list of available MOFs by CVD and MLD approaches.

The possibility to form MOFs and organic-inorganic coordinated networks from the gas-phase makes them compatible with vacuum technologies and more generally the
fabrication processes in microelectronics. Ivo Stassen et al. developed CVD approach to deposit a high-quality and uniform MOF, converting an ALD-deposited ZnO thin film with 2-methylimidazole (HMIM) vapor to MOF zinc-(2-methylimidazolate)\(_2\) (ZIF-8) [109]. As a first showcase of applicability of the process in microelectronics, the group of Rob Ameloot applied additive lithography, also known as lift-off patterning, for structuring of the MOFs (figure 20(a)). Therein, zinc oxide was deposited by reactive sputtering, rather than ALD, and converted to ZIF-8 from the gas phase. Since the MOF-CVD process of zeolitic imidazolate frameworks-8 (ZIF-8) is entirely solvent-free, there are no risks of distorting the photoresists and losing the pattern during the lift-off process. The achieved resolution of the pattern of 1.7-\(\mu\)m was the best photolithographically defined MOF pattern at that time (figures 20(b), (c)). Another showcase relied on conformal coating of elastomeric pillar arrays, which can be used for stem cell stimulation, microfluidic sensing, and biomimetic adhesives (figure 20(d)). MOF-CVD coating did not disturb the structural integrity of the pillars (figure 20(e)), while the corresponding wet chemical process for ZIF-8 lead to a undesired collapse of the structures (figure 20(f)) [110]. Earlier studies used a wet-chemical approach and demonstrated the potential applicability of ZIF-8 for \(H_2\) storage or as electrodes in electrical double-layer capacitors (EDLCs) [111].

The MOF-CVD approach was extended to ZIF-67 from CoO\(_2\) by Krishtab et al. [112]. Both ZIF-8 and ZIF-67 show a Young’s modulus and a dielectric constant comparable to state-of-the-art porous organosilica dielectrics, making them attractive for advanced on-chip interconnects. A further example for an all-gas-phase process is the growth of Zr(IV)-based UiO-66 by MLD [113]. The group of Ola Nilsen applied MLD using ZrCl\(_4\) and 2-amino-1,4-benzene dicarboxylic acid (2-amino-1,4-BDC) as precursors [113]. They achieved control over the crystallinity of the hybrids with exposure of the as deposited amorphous film to acetic acid vapor or post-annealing. Previous studies applying wet chemical synthesis showed that UiO-66 might be used for gas storage [114], catalysis [115], or decomposition of tosins [116].

The group of Maarit Karppinen developed novel ALD/MLD processes for coordination network terephthalate (TP) thin film fabrication including calcium-terephthalate [29], iron-terephthalate [117], lithium-terephthalate [15], copper(II)terephthalate [118], lanthanum-terephthalate and the entire family of s-block metals (Li-TP, Na-TP, K-TP, Ba-TP, Mg-TP, Ca-TP, and Sr-TP) [119]. Besides, MLD allows to post-synthetically introduce metals or hybrid clusters into MOFs. Recently, copper dicarboxylate MOFs were obtained with an out-of-plane orientation of the pores, which makes them easily accessible for posterior loading [120]. With volatile precursors, small enough to penetrate the porous structure of the MOFs, it is possible to deposit novel iron thiolate clusters inside the MOF NU-1000 [121]. In this MOF/organic assembly, iron thiolate clusters act as a light-induced nitrate reduction catalyst.

7.4. Hybrid materials for battery applications

Energy storage is today a key issue that enables all conveniences in our society, including the use of mobile phones and laptops, driving electric cars, storing solar energy, etc. Lithium-ion batteries (LIB) play an utmost important role. This is attributed to their high specific capacity and low self-discharge properties. LIBs are commonly used in electric vehicles, foldable electronics, medical sensors and further mobile devices. Therefore, there is a great demand for fast-charging batteries, which do not degenerate too quickly upon charging-discharging and, even more importantly, do not have safety issues, as metallic Li, as it is used in batteries, is highly reactive [122].

Until recently, vapor phase deposition techniques were relatively unexplored for battery applications, except for ALD. ALD serves in various ways to enhance the efficiency of the batteries [123]. First, the chemically active ternary materials with high specific capacity can be deposited on high surface area 3D nanostructures to serve as anode [124, 125]. Furthermore, ALD coating can also be applied to electrodes to improve the separator’s performance. Protective and conformal thin films on an anode function as an artificial solid electrolyte interface (SEI), reducing the capacity degradation and enhancing the cycling stability and Coulombic efficiency of the resulting battery [126]. Additionally, sub-nanometer coatings on cathodes can prevent their dissolution into the reactive electrolyte. MLD, following the conformal nature of ALD, attracted attention in the field of energy-related applications. Except for the exceptional quality of the MLD thin films, hybrid organic-inorganic materials can inherit the advantageous mechanical properties from their organic constituents and combine those with the optical, chemical, and electrical properties of the inorganics due to synergistic effects [127]. One of the first reports involving MLD has already shown promising results, especially in the field of novel organic electrode materials as described in the following.

Recently, organic electrode materials attracted increasing attention as cheap, environmentally friendly low-weight alternative to traditional metal-based inorganic electrodes. They have undeniable benefits for a use in flexible batteries or supercapacitors. The group of Karppinen was the first to demonstrate the growth of hybrid structures of lithium terephthalate (Li\(_2\)C\(_6\)H\(_4\)O\(_2\) or LiTP) ALD/MLD, which were employed as anode material, as LiTP possesses a high specific energy and gravimetric capacity as well as a relatively small volume change during (de)lithiation [128]. Gas-phase grown LiTP films appeared to be electrochemically active with an excellent rate capability even without conductive additives. A stabilization of the structures with a protective ALD layer of LiPON resulted in a capacity retention of over 97% after 200 charge/discharge cycles at 3.2 C.

Some metalcones can also serve as organic electrodes for LIBs. The group of Detavernier demonstrated the applicability of titanicones as electrochemically active material [129]. Two novel processes were studied for the titanicone MLD grown
from tetrakisdimethylaminotitanium (TDMAT) and glycerol (GL) or ethylene glycol (EG) as precursors. Upon using EG as the most common organic precursor for metalcones, the growth terminated after the initial 10 cycles, which was explained with double surface reactions of EG and the resulting saturation of surface functionalities. At the same time, the TDMAT/GL process showed a linear growth behavior versus cycle number. An annealing step at 500 °C in a He atmosphere induced lithium-ion conduction during cyclic voltammetry. Interestingly, with increasing charge current, the capacity retention of the He-annealed samples outperformed that of the amorphous and anatase TiO$_2$ references. Similar research was performed for vanadicones, grown by MLD from tetrakisethylmethylaminovanadium (TEMA V) and GL or EG [130]. A linear growth as a function of the number of cycles was achieved only with the TEMAV/GL process, but not with EG. The resulting hybrids were annealed in an inert He atmosphere to activate the vanadicones chemically, and also to retain their carbon content. The annealed samples showed improved capacity and performance over the pure inorganic V$_2$O$_5$ films in the 1.0 to 3.5 V vs. Li$^+$/Li range. Moreover, vanadicones have an excellent cyclability, their Coulombic efficiency was measured with 99.2%, and their capacity increased over the course of the first 100 charge/discharge cycles. A further type of metalcones, manganicones, which are manganese alkoxide films (MnEG), demonstrated their great potential for a use as cathode material in thin-film Li-ion batteries and as catalyst for electrochemical water splitting [131]. Incorporating organic moieties into manganese oxide thin films stabilizes the film and suppresses its restructuring, which is typically observed after electrochemical cycling of inorganic manganese oxides. Restructuring is a severe issue which may lead to catastrophic device failure. Therefore, its suppressing is a step that contributes to the safety of LIB. Interestingly, the inherent catalytic activity of manganicone remained on the same level as that of pure inorganic manganese oxide.

The safe performance of LIBs is crucial for implementation into advanced portable electronic devices and electric vehicles. Metallic lithium, even though it is considered ideal as anode for LIBs, has key technical issues. Among other, those include the growth of needlelike dendrites upon cycling, caused by nonplanar electrodeposition. Such dendrites can spike the separator and short cut the cell. Another challenge is associated with an electrolyte depletion, caused by a parasitic reaction between the lithium metal and the electrolyte, leading to capacity fading, gradual electrolyte consumption and battery failure. To tackle these problems, the group of Elam grew a 6-nm thick MLD alucone thin film directly on the lithium electrode [132]. They discovered that the alucone coating helped to achieve a several times longer cycle life at high current rates than uncoated lithium and that the resulting battery yields a stable Coulombic efficiency of 99.5%. In another battery setup, the lithium sulfur batteries (Li-S), an alucone-protected anode also improved the performance of the Li-S batteries. The capacitance reached 657.7 mAh g$^{-1}$, and the improvement of the performance over the corresponding bare Li-S battery was 39.5%. Further work that applied alucone to various electrodes includes Li-LiCoO$_2$ systems[133], Si anodes [134], Na anodes [135], and C/S cathodes [136]. Given all those encouraging results, MLD appears to be an effective tool for sustaining a stable and safe operation of batteries.

Figure 20. MOF integration routes enabled by the MOF-CVD process: lift-off patterning and coating of fragile features. (a) Schematic diagram of MOF pattern deposition by MOF-CVD and subsequent lift-off of a patterned photoresist. (b), (c) Scanning electron microscopy images of the manufactured ZIF-8 patterns. (d) Schematic diagram of the production of ZIF-8-coated polydimethylsiloxane pillars by soft lithography and MOF-CVD. (e) Scanning electron microscopy image of MOF-CVD-coated PDMS pillars. (f) Scanning electron microscopy image of identical PDMS pillars after conventional solution processing of ZIF-8. The MOF-CVD processing steps are indicated with a dashed line in a and d. Oxide and MOF films are represented in red and blue, respectively. Scale bars, 100 µm for b, 10 µm for c, 20 µm for e,f, 1 µm for insets. Reprinted by permission from Springer Nature Customer Service Centre GmbH: Nature, Nature Materials, [109]. Copyright © 2015, Springer Nature.
8. Conclusions and perspectives

Materials science has seen a considerable push towards the creation and tailoring of hybrid materials, which opt for enabling the next generation of applications and technologies. Purely organic or inorganic materials are unlikely to be able to fulfill the future needs.

Vapor phase processes of various types are among the most appealing strategies for the synthesis of such functional hybrid materials for a variety of reasons. On the one hand, many processes may show compatible with currently applied processes in various industrial branches, and on the other hand, the nature and functionality of the materials created by vapor phases processes often show differences to wet chemically synthesized hybrids, in spite of the similarity in composition. Therefore, vapor phase processes may not act as substitute for wet chemical processes only, but also add value for the tailoring of the functionalities.

The various vapor phase processes are at this stage being explored and interesting material combinations are being evaluated. Those include true hybrid materials, so-called metalcones, which are grown bottom-up with ALD and MLD, polymer-inorganic hybrids created upon infiltration of polymers with inorganics, or laminate structures or MOFs fabricated by means of CVD, ALD, MLD or other vapor phase techniques. The resulting materials, typically thin films, showed a plethora of interesting properties which may demark a first step towards fabrication of new flexible electronic devices, biosensors, functional textiles or biomedical implants. In many cases the properties outperform those observed from non-hybrid materials, that is, materials which rely on a singular composition, inorganic or organic. The interplay between different materials classes often results in synergy, meaning that certain properties are significantly better than the sum of the properties of the components. Such cases are of great interest for each application field, since the neat contributing components may never reach such an enhanced level of functionality. But even if there is no enhancement, but only a sum of functionality, such nanocomposites can also be of great value, simply for the coexistence of the desired properties of each material. However, one must be aware that a number of hybrid materials will also show the opposite effect. A loss in functionality might be observed in cases where interactions of metal with polymers result in embrittlement, draining of charge carriers, etc. Therefore, a significant effort will be needed for the further development and improvement of such materials, ideally with strong contribution from machine learning.

The wide spreading of the fields of investigation indicates the paramount interest of the various industries in such flexible and optically, electronically or biomedically functional materials. The trend towards investment into research and development of hybrid materials is very obvious, not at least from the industrial collaborations of many of the researchers whose work was reviewed here. Specifically, the sectors of electronics, biomedicine and energy are expected to highly benefit from the future developments, both in instrumentation development and materials development, in near future. But also, the very early results shown in this review might trigger new ideas towards creation of functional materials for later generations of technologies, for example quantum computing or similar.

The research field is already very active and the activity is currently steadily increasing, thus plenty new and amazing results are expected in the field of hybrid materials, specifically vapor phase processed ones, in the forthcoming years.

Author contributions

All authors contributed to the write-up of this topical review to the same amount.

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