Perspective

High-Throughput Synthesis of Thin Films for the Discovery of Energy Materials: A Perspective

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ABSTRACT: Thin films are an integral part of many electronic and optoelectronic devices. They also provide an excellent platform for material characterization. Therefore, strategies for the fabrication of thin films are constantly developed and have significantly benefited from the advent of high-throughput synthesis (HTS) platforms. This perspective summarizes recent advances in HTS of thin films from experimentalists' point of view. The work analyzes general strategies of HTS and then discusses their use in developing new energy materials for applications that rely on thin films, such as solar cells, light-emitting diodes, batteries, superconductors, and thermoelectrics. The perspective also summarizes some key challenges and opportunities in the HTS of thin films.

High-Throughput Synthesis of Thin Films

Fragmentary (discontinuous) — Micro-pipetting, Spin coating

Gradient (continuous) — Slot-die coating, Sputtering, Physical-Vapor Deposition

KEYWORDS: high-throughput, thin films, material discovery, combinatorial optimization, perovskites, energy materials, batteries, superconductors
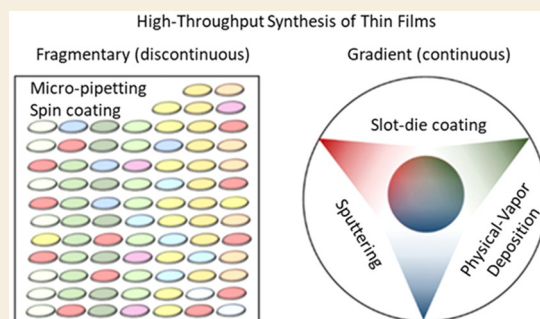
INTRODUCTION

The pace of development of new technologies is often dependent on the advent of new functional materials. To accelerate the exploration of new materials, high-throughput synthesis (HTS) techniques are being developed to discover new compositions or to optimize known ones.[1−6] Figure 1a depicts the main stages of high-throughput material discovery in a closed-loop manner: high-throughput synthesis,[7] high-throughput data mining (i.e., characterization[8]), and data analysis.[4,9−15]

Data mining is essential to evaluate synthesized materials. Thanks to rapid spectroscopy and electrical characterization techniques, high-throughput quantification of materials' many important figures of merit, such as band gap,[16] conductivity, charge carrier concentration, and mobility, became possible.[17] High-throughput methods of structural and compositional analysis remain to be developed.

Data analysis is essential to uncover patterns within large data sets using statistical analysis. The use of machine learning algorithms is now of high interest for organizing and filtering data and eventually for modeling the target data set or predicting the outcomes of the next experiments.[18] High-throughput data mining and data analysis are not a focus of this work and have been discussed elsewhere.[19,18]

A key focus of this perspective, high-throughput synthesis, is arguably the most important step in the high-throughput discovery of materials.[7,8,20−22] HTS is essential for creating a high-quality data set that eventually determines the accuracy and efficiency of material discovery. Variations of HTS have
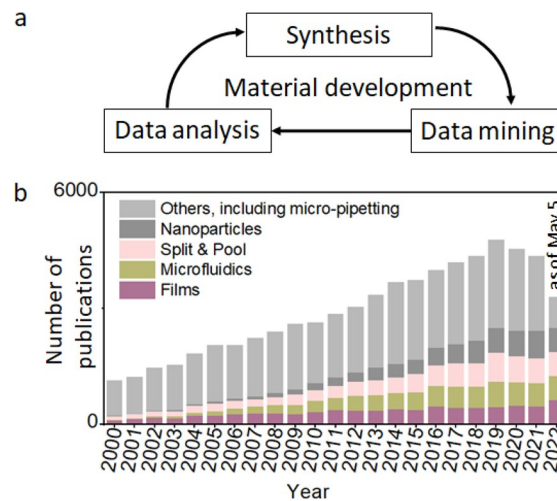

Figure 1. High-throughput discovery of materials. (a) Three-step closed-loop optimization and discovery of materials. (b) Number of publications on HTS platforms extracted from the Web of Science using the keywords "throughput or combinatorial" and synthetic techniques, such as "fluidic or microfluidic", "split or pool", "nanoparticles", and "films". A decrease in the number of publications in 2020 and 2021 is likely due to the COVID-19 pandemic.
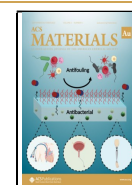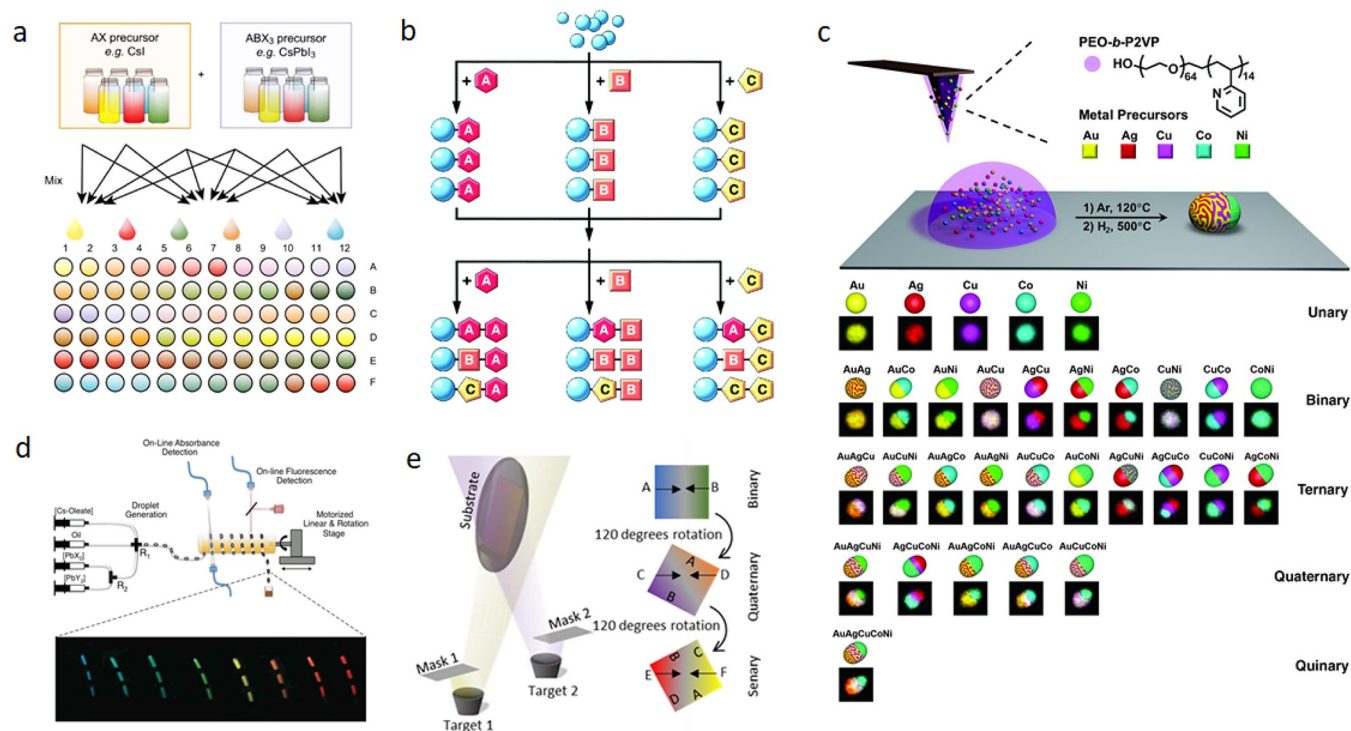
Figure 2. Schematic of various HTS platforms. (a) Micropipetting platform. Reprinted in part with permission under a Creative Commons CC BY License from ref 47. Copyright 2021 Springer Nature. (b) Split and pool technique. Reprinted in part with permission from ref 40. Copyright 2001 Wolters Kluwer Health, Inc. (c) Scanning probe block copolymer lithography. Reprinted with permission from ref 44. Copyright 2016 The American Association for the Advancement of Science. (d) Microfluidic platform. Reprinted with permission under a Creative Commons CC BY License from ref 48. Copyright 2016 American Chemical Society. (e) Physical-vapor deposition. Adapted with permission from ref 49. Copyright 2021 Elsevier.

been used for a long time in the solid-state peptide synthesis[23] and codeposition[24−26] of ternary alloys such as Fe-Cr-Ni[27] as well as drug discovery[28−30] and pharmaceutics.[31] Among HTS techniques, microfluidics, split and pool, and micropipetting have been dominant platforms (Figure 1b). The other common HTS platform is based on thin films created by various deposition methods such as sputtering, evaporating, and spraying. Though less explored (Figure 1b), the HTS of thin films offers some unique opportunities. First, material characterization techniques are usually well-suited for application to thin films. Second, many devices rely on the development of thin films. For example, typical thin-film solar cells are made of at least five thin films, including two electrodes, a light-absorber semiconductor, and two charge-carrier-selective materials.[32]

This perspective discusses recent advances in the HTS of thin films. We first briefly summarize major HTS techniques and then focus on the HTS of thin films. We will then discuss the HTS of thin films that are applied to explore materials for energy-related applications, such as solar cells, light-emitting diodes (LEDs), batteries, thermoelectrics, and superconductors. To the best of our knowledge, there are only a few review and perspective papers on HTS of thin films focusing on physical-vapor deposition of metals[33] or organic solar cell materials.[1] This perspective instead emphasizes HTS of thin films by solution-processed techniques for a broader family of energy-related materials. It is worth noting that this perspective does not intend to cover all known thin-film HTS methods, but it rather focuses on recent and illustrative approaches and emphasizes the importance of thin-film platforms in the discovery of new materials.

HIGH-THROUGHPUT SYNTHESIS PLATFORMS

Figure 2 illustrates common platforms of HTS of materials. We will now briefly discuss each of these methods and then focus on the HTS of thin films. Figure 2a shows the principle of the micropipetting platform that allows dispensing of several components into 72 reservoirs or wells. These miniaturized reactions are widely used to crystallize proteins from hundreds of precursor combinations at a time.[34−38] This method was also recently used to synthesize halide perovskites, a promising emerging family of materials for optoelectronic applications. The outcomes were characterized by convolutional neural network-based image recognition, which led to the first synthesis of $(3\text{-PLA})_2PbCl_4$ with a strong blue photoluminescence.[38]

Figure 2b displays the split and pool synthesis, in which two or more compounds are first mixed to prepare a pool and then divided into several segments. Each of these segments is then mixed again with new building blocks.[39,40] The stepwise iteration in the split and pool approach allows making millions of compounds as mixtures.[41−43] The split and pool HTS is widely used in high-throughput synthesis and analysis of proteins and RNAs.[43]

Figure 2c shows a dip-pen lithography approach to synthesizing nanoparticles in a high-throughput manner.[44] Attoliter-scale volumes of multiple precursors are delivered to the desired location where a chemical reaction is then induced. The method has been widely used for making bimetallic nanoparticles[45] and even a single trimetallic alloy nanoparticle.[46] It was also used for combinatorial synthesis of nanoparticles consisting of five different elements (Au, Ag, Cu,
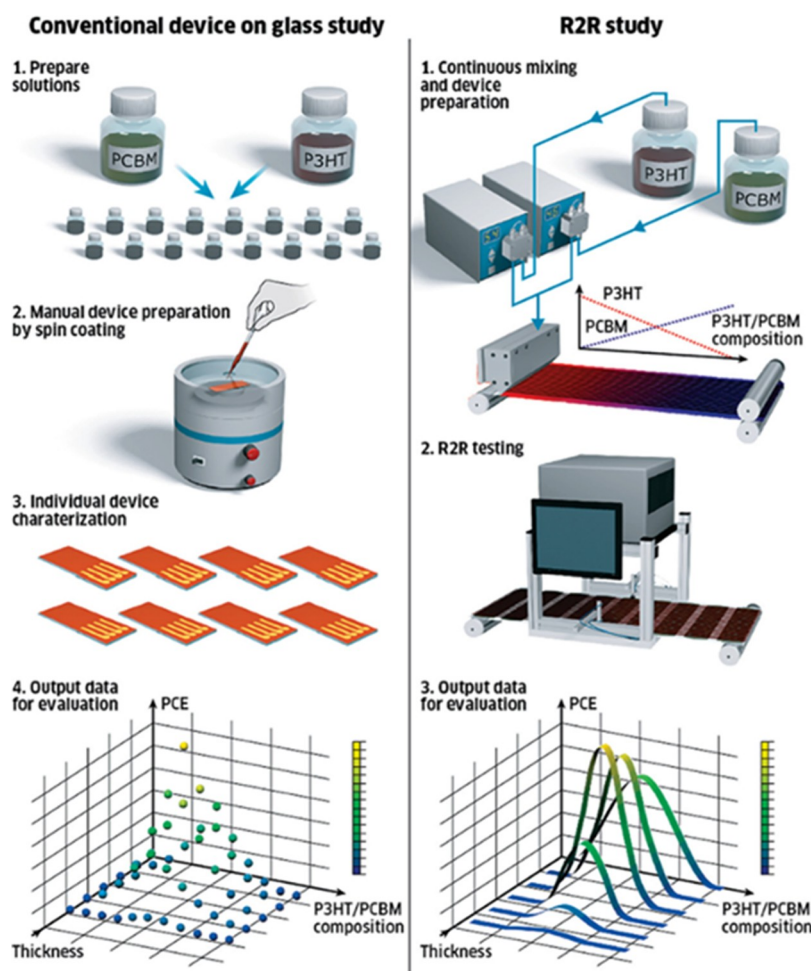
Figure 3. Fragmentary vs continuous-composition high-throughput synthesis of organic thin films. Reprinted with permission from ref 62. Copyright 2010 American Chemical Society. The left panel depicts the preparation of thin-film libraries by the fragmentary approach in which distinct thin-film compositions are made and studied. The right panel depicts the preparation of thin-film libraries by a continuous optimization approach in which the thin-film composition is graded across the film. PCBM stands for phenyl-C61-butyric acid methyl ester, P3HT stands for poly(3-hexylthiophene-2,5-diyl), PCE stands for power conversion efficiency of solar cells, and R2R stands for roll-to-roll processing.

Co, and Ni): in this case, polymers with preloaded metal salts were deposited onto a substrate and then thermally annealed to create nanoparticles (Figure 2c).

Figure 2d demonstrates a microfluidic platform[50−53] that allows containing and controlling fluids in micrometer dimensions in a spatiotemporal manner.[48] The controlled coflowing through the microfluidic channels leads to interfaces or mixed solutions where chemical reactions may occur.[54,55] Microfluidic-based HTS is widely used to synthesize nanoparticles and to discover drugs.[56] A microfluidic platform was recently used to study the crystallization of cesium lead halide perovskite nanocrystals.[48] The nucleation mechanism of perovskite nanocrystals was found to be similar to metal chalcogenide systems, but with much faster reaction kinetics.[48] The microfluidic platform can also be applied to build asymmetric bilayers using naturally derived lipids that mimic mammalian cells, which then were used to quantify the effect that lipid asymmetry has on the permeability of doxorubicin, an anthracycline class of chemotherapy drugs.[57]

Figure 2e shows one of the common methods of creating material libraries based on thin films by physical-vapor deposition from multiple target materials. In this method, mask positioning can lead to compositionally graded thin films,

also termed continuous-composition optimization, in which all possible binary or even multinary alloys are synthesized (Figure 2e).[33] The moving mask in different angles leads to the formation of gradient films on a substrate.[49] Rotation of the substrate by 120° in each codeposition process and controlling the speed of the mask allow making thin-film alloys from up to six components (Figure 2e). Thus-made gradient thin films allow exploration of full composition and process parameter spaces (Figure 3, right panel)[58] and material interfaces and thicknesses.[59]

Solution-processable methods are also used to make a library of materials based on thin-film platforms, among which spin-coating is the most common. Spin-coating implies depositing films from many solutions premade by discrete mixing of precursors, also termed fragmentary (or discontinuous) composition optimization (Figure 3, left panel). Since the fragmentary approach is discontinuous and, hence, misses intermediate compositions, computational tools are usually used to simulate the entire parameter space.[60]

In contrast, continuous-composition optimization can cover the entire parameter space (Figure 3, right panel). This can be realized in compositionally graded films made by physical-vapor deposition (Figure 2e) or solution-processed techniques

Table 1. Characteristics of HTS Platforms

HTS platforms	Composition continuity	Synthesizing methods		Number of components to be optimized	Solid-state device compatibility
		Solution	Physical-vapor deposition		
Micropipetting	Fragmentary	Yes		High	No
Nanoparticles	Fragmentary	Yes		High	No
Split and pool	Fragmentary	Yes		High	No
Microfluidics	Fragmentary/Continuous	Yes		Limited	No
Thin Films	Fragmentary/Continuous	Yes	Yes	Limited	Yes
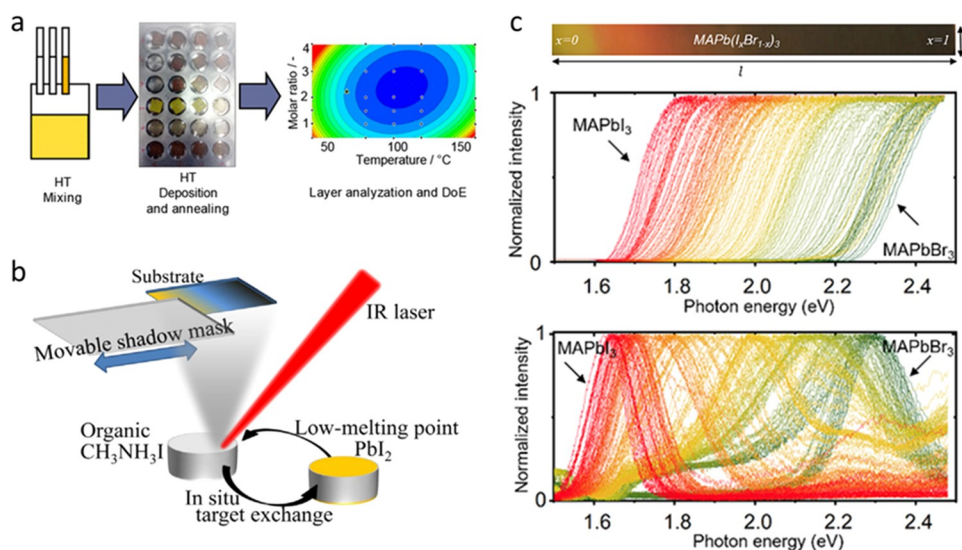
Figure 4. Fragmentary vs continuous high-throughput synthesis of perovskite thin films. (a) Fragmentary HTS of thin films made by spin-coating. Reprinted with permission from ref 60. Copyright 2020 American Chemical Society. (b) Continuous compositionally graded films synthesized by coevaporation of two precursor materials. Adapted with permission under a Creative Commons CC BY License from ref 65. Copyright 2017 Taylor & Francis. (c) Top view of a perovskite compositionally graded film (top panel) made by slot-die coating of two precursor inks and characterized by absorption (middle panel) and photoluminescence (bottom panel) spectroscopy. Reprinted with permission under a Creative Commons CC BY License from ref 16. Copyright 2022 Springer Nature.

such as slot-die coating (Figure 3, right panel). In the latter, two precursor inks are supplied into a slot-die reservoir, where the inks are mixed and deposited on a substrate as a thin film. Because the supply rate of one ink is increased over time, while the second one is decreased, this approach leads to the in situ change of composition (Figure 3, right panel) and eventually compositionally graded films. The use of this method in the optimization of organic and perovskite solar cell materials is discussed below.[16,60]

Although an objective comparison of all discussed HTS platforms is challenging, the following can be said (Table 1). Microfluidic and thin-film HTS platforms enable continuous-composition optimization, but they are limited to multiple components. For optimizing multicomponent compositions, nanoparticle and split and pool HTS platforms are best suited. Thin-film platform's ultimate products are thin films that land themselves for device integration.

■ APPLICATIONS OF THIN FILMS MADE BY HTS

In this section, we will discuss the use of HTS of thin films in the development of novel materials for applications in energy capture (solar cells and thermoelectrics), energy storage (batteries), and energy transport (superconductors).

Solar Cells

Emerging solar cells suffer from either low performance or stability.[61] Since they are made of multiple layers of thin films and each film is usually made of complex multinary

components, their composition and fabrication strategies are constantly explored to address the mentioned challenges.

The common approach for the high-throughput exploration of solar cell materials is fragmentary (or discontinuous) optimization of composition. Figure 4a illustrates examples fragmentary optimization in which different precursor ratios are used to make a library of organic and perovskite films, respectively,[62,60] which then were used to study their performance and stability. In another work,[63] a machine learning algorithm was used to optimize over 100 processing variations in fabricating organic photovoltaic devices. The fragmentary approach was also adopted for inkjet printing of homogeneous compositions of $CsPb(Br_xI_{1-x})_3$.[64]

Continuous-composition optimization was also used for the exploration of solar cell materials. For instance, a pulsed infrared semiconductor laser was adopted for thermal evaporation of perovskite precursor CH_3NH_3I/PbI_2 bilayer films, where the thickness of each layer was controlled to achieve gradient composition (Figure 4b).[65] A movable mask system was used to deposit combinatorial thin-film libraries.[65] The synthesized films were used to fabricate solar cells and study the dependence of photovoltaics efficiency from precursor stoichiometry and thickness. Similarly, other works used compositionally graded thin films for optimization of organic or hybrid photovoltaic materials.[66,36,67−69]

We recently developed a solution-processed approach for fabricating compositionally graded films.[16] Our approach uses
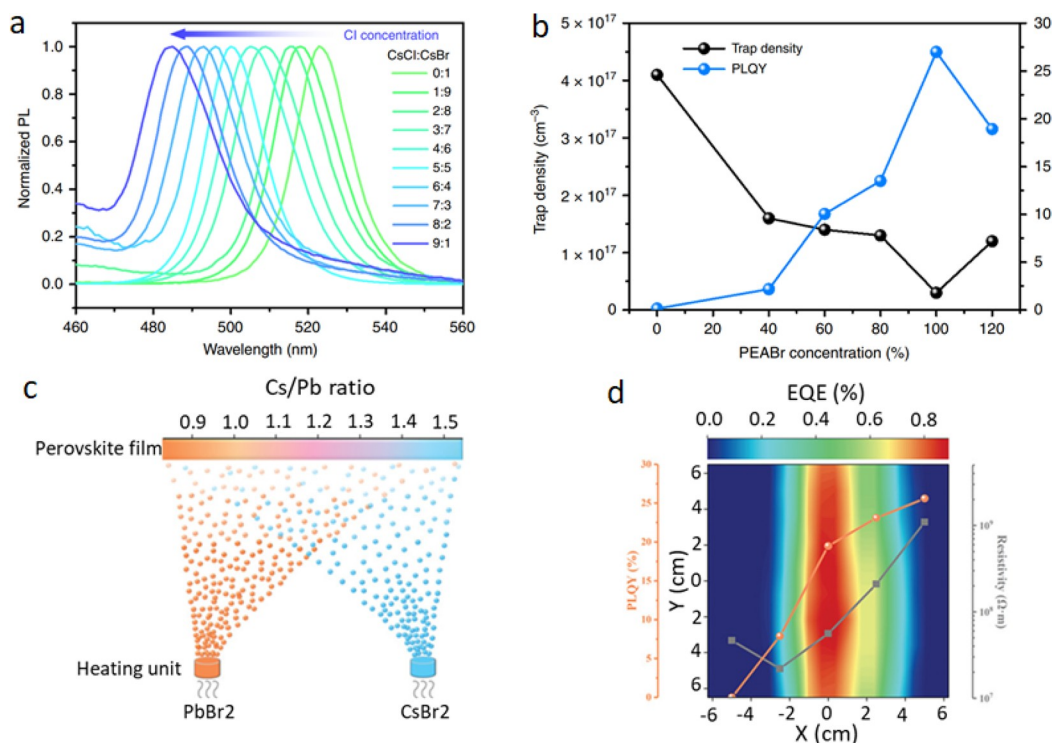
Figure 5. Fragmentary vs continuous high-throughput synthesis of perovskite thin films for LEDs. (a) Photoluminescence (PL) spectra of CsPbCl$_x$Br$_{3-x}$ thin films with different molar ratios of CsCl to CsBr. Reprinted with permission under a Creative Commons CC BY License from ref 73. Copyright 2019 Springer Nature. (b) Trap densities and photoluminescence quantum yields (PLQYs) of CsPbCl$_{0.9}$Br$_{2.1}$ thin films with different ratios of phenylethylammonium bromide (PEABr). Reprinted with permission under a Creative Commons CC BY License from ref 73. Copyright 2019 Springer Nature. (c) Schematic of dual-source coevaporation deposition for a perovskite film. Reprinted with permission from ref 74. Copyright 2019 John Wiley and Sons. (d) Spatially resolved external quantum efficiency (EQE) mapping of assembled devices; photoluminescence quantum yield (PLQY) and resistivity of perovskite films. Reprinted with permission from ref 74. Copyright 2019 John Wiley and Sons.

slot-die coating with two pumps, each programmed to supply different solutions in a gradient rate in order to in situ change the output composition. Figure 4c illustrates an example of our compositionally graded film prepared from MAPbI$_3$ and MAPbBr$_3$ perovskites. The transition of color from pure MAPbI$_3$ (black) into pure MAPbBr$_3$ (orange) indicates the linear gradient composition of MAPb(I$_x$Br$_{1-x}$)$_3$. The film was characterized by measuring absorption and photoluminescence spectra in >200 locations, indicating a gradual shift of band gap across the film (Figure 4c). Access to the compositionally graded films has also enabled the observation of three distinct degradation mechanisms of perovskite alloys, depending on halide content: iodide-rich perovskites degraded through desorption of the organic component, bromide-rich perovskite through hydration, and all intermediate alloys through phase segregation.[16] Stabilization of perovskite materials and solar cells is a subject of intense investigation.

Light-Emitting Diodes

Replacing inefficient conventional light sources, which utilize one-third of electricity globally,[70] with power-saving LEDs could play a major role in the conservation of energy. LEDs based on perovskites offer high external quantum efficiency, pure colors, and tunable emission spectra.[71] However, the most-wanted blue perovskite LEDs suffer from low performance compared to red and green ones.[72] HTS platforms are currently used to discover stable and efficient blue LEDs.

Figure 5a and b shows a fragmentary approach for optimizing blue-emitting perovskite thin films.[73] Through

composition engineering by incorporating Cl into the CsPbBr$_3$ lattice, the work first finds that the perovskite of CsPbCl$_{0.9}$Br$_{2.1}$ composition offers a blue emission centered at 484 nm. Phenylethylammonium bromide is subsequently introduced into the CsPbCl$_{0.9}$Br$_{2.1}$ perovskite to passivate the traps and improve the photoluminescence quantum yield from 0.15% to a maximum of 27%.

Figure 5c and d shows a continuous approach toward optimization of the perovskite composition for LEDs.[74] The work uses dual-source physical-vapor deposition of CsBr and PbBr$_2$ to prepare continuous gradient films. The Cs/Pb ratio in the perovskite film gradually changes from one part to another part of the film. The observed trend of device efficiency is explained as a trade-off between photoluminescence quantum yield and injection efficiency (resistivity): samples with high injection efficiency (low resistivity) and low photoluminescence quantum yield (and vice versa) lead to low LED efficiency. The LED performs best when these two figures are balanced, which is achieved in samples with a Cs/Pb ratio of 1.17/1.

Batteries

There is an urgent need for high-capacity, low-cost, and stable energy storage devices. Thin films can offer a critical platform for screening the desired properties of battery materials such as ionic diffusivity, capacity, phase stability, and volume expansion.[75] HTS of thin films is widely used in the development of anodes,[76] cathodes,[77] solid electrolytes,[78,79] and organic electrode materials.[80]

The fragmentary HTS approach is common in synthesizing multinary battery material compositions. High-throughput sol–gel synthesis was earlier used to optimize the magnesium doping concentration for lithium ferrophosphate ($LiFePO_4$), a material of great interest as a safe, environmentally friendly cathode for lithium-ion batteries (Figure 6a).[81] The work has
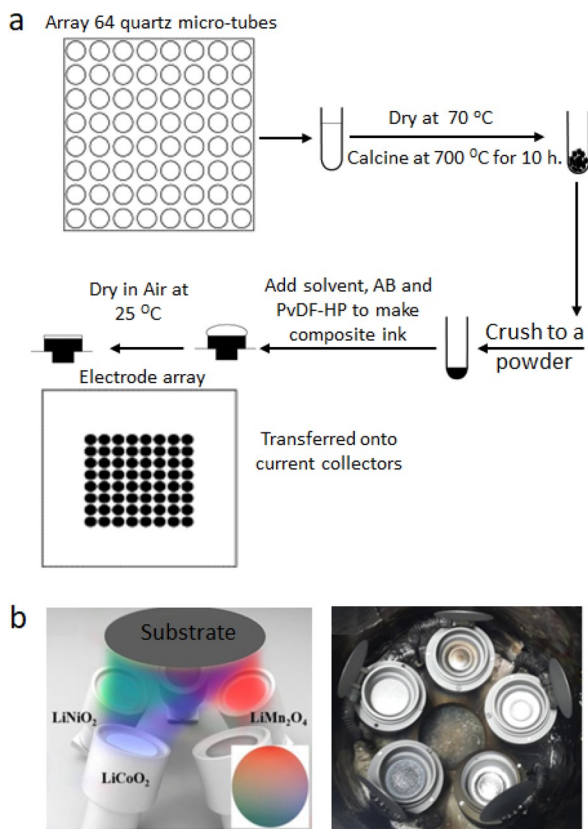
Figure 6. Fragmentary vs continuous high-throughput synthesis of thin films for battery applications. (a) Fragmentary HTS of $LiFe_{(1−y)}Mg_yPO_4$ and $Li_{(1−x)}Mg_{x/2}FePO_4$. Reprinted with permission from ref 81. Copyright 2008 Elsevier. (b) Continuous compositionally graded films synthesized by codeposition of five precursors; schematic of the composition gradient across the substrate in the left panel and five target sputter deposition chamber setup in the right panel. Reprinted with permission from ref 26. Copyright 2016 Elsevier.

shown that magnesium substituted for iron in the precursor mixture ($LiFe_{(1−y)}Mg_yPO_4$) showed better battery performance than when magnesium substituted for lithium in the precursor mixture ($Li_{(1−x)}Mg_{x/2}FePO_4$). A similar approach has been utilized for optimizing sodium-ion battery cathodes, particularly the Na-Fe-Mn-O pseudoternary system of high immediate interest.[82]

The other approach of HTS of battery materials is gradient codeposition of battery materials. Figure 6b shows a schematic of using five magnetron sources for sputtering targets with a radio frequency switching to prepare a library of Li-$[Ni_xCo_yMn_z]O_2$ alloys.[26] The study found that Mn-rich compositions showed higher discharge capacity retention and stability than Ni-rich battery compositions.

Superconductors

The lack of an extensive material library of superconductors makes it challenging to investigate the mechanism of much-needed high-temperature superconductivity. HTS platforms

could provide access to a more comprehensive library of superconductive materials.[83]

Figure 7a illustrates an example of the preparation of a superconductor material library. $Fe_{70}Co_{30}$ and V alloys using a
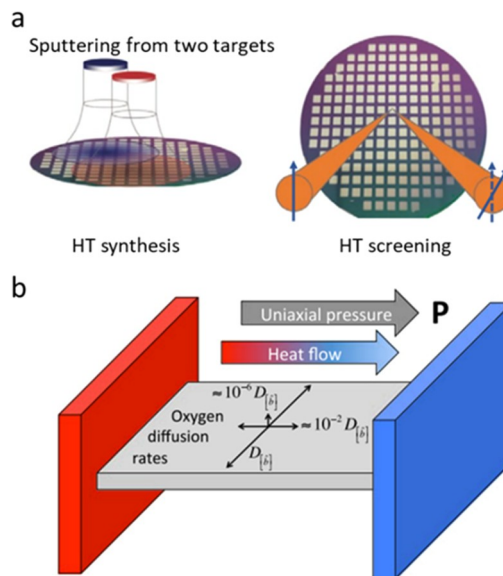
Figure 7. Fragmentary vs continuous HTS of thin films for superconducting materials. (a) Fragmentary cosputtering $Fe_{70}Co_{30}$ and V synthesis. Reprinted in part with permission under a Creative Commons CC BY License from ref 84. Copyright 2017 Taylor & Francis. (b) Continuous compositionally graded $YBa_2Cu_3O_{\triangledown x}$. Reprinted with permission from ref 87 Copyright 2017 IEEE.

shadow mask were deposited on a film grid.[84] Then hysteresis loops across the material library were measured. The cosputtering technique with a gradient deposition was also used in studying the Fe-B binary system on a Si wafer.[85,86]

Figure 7b depicts a schematic of a continuous-composition-gradient film made of high-temperature superconducting compound $YBa_2Cu_3O_{\triangledown x}$, wherein the oxygen content (x) spatially varies across the length of the sample.[87] The $YBa_2Cu_3O_x$ films were grown on a ⟨001⟩ $SrTiO_3$ substrate using the pulsed laser ablation method.[88] The continuity nature of the oxygen pressure and thermal effects along the film enable the fabrication of this graded film.

Thermoelectrics

Thermoelectric materials are generally used in bulk form, but thin films can offer a platform for optimizing thermoelectric properties such as thermal diffusivity, carrier mobility, Seebeck coefficient, and other figures-of-merit as a function of chemical composition.[89] The limited number of known thermoelectric materials and their low efficiency demand HTS techniques to discover and develop novel thermoelectric materials.

Synthesis of a gradient film from a ternary system ($CoSb_3$-$LaFe_4Sb_{12}$-$CeFe_4Sb_{12}$) made by pulsed laser deposition was earlier reported,[90] as was a thermoelectric screening tool (Figure 8a) capable of performing a temperature-dependent study spatially measuring the continuous gradient film's Seebeck coefficient and electrical resistivity (Figure 8b).[90] HTS of thin films was also applied to study several other thermoelectric materials such as $(Ca_{1−x−y}Sr_xLa_y)_3Co4O_9$,[91] Ti-Ni-Sn,[92] and Al-Fe-Ti.[93]
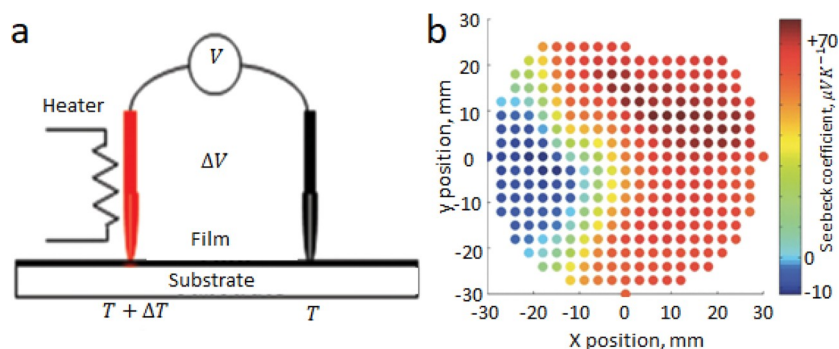
Figure 8. (a) High-throughput temperature-dependent Seeback coefficient screening tool. Reprinted with permission from ref 90. Copyright 2013 AIP Publishing. (b) Seebeck coefficient contour plots for a ternary $CoSb_3$-$LaFe_4Sb_{12}$-$CeFe_4Sb_{12}$ combinatorial film deposited on a quartz wafer. Reprinted with permission from ref 90. Copyright 2013 AIP Publishing.

CONCLUSIONS AND OUTLOOK

Developing HTS of thin films is important to accelerate the exploration and investigation of much-needed new materials to address some global challenges such as accessible and renewable energy capturing, storage, and transport. Thin films offer a unique platform for HTS of multicomponent compositions. Thin films are also compatible with many commercial devices. As discussed above, fragmentary (discontinuous) alloy optimization is most widespread, but it misses intermediate compositions. In contrast, compositionally graded films cover all the possible alloys and, hence, offer access to the entire parameter space. The following challenges and opportunities exist in the HTS of thin films.

Synthesis of multinary compositions (containing three or more components) on a substrate is a challenge. In this regard, evaporation techniques with controllable parameters such as deposition speed, movable masks, and substrate rotation enable printing up to senary (six components) phases. The gradient films with a higher number of components are harder to make, but microfluidic platforms that store all-compositional spaces may allow printing of multinary compositions.

Another challenge is improper mixing of precursors, leading to inhomogeneous thin films due to local phase segregation. A proper mixing can be achieved by coevaporation (for physical-vapor deposition) and turbulent flow of inks (for solution-processed deposition). This is particularly a challenge for physical-vapor deposition techniques in which a slow process may lead to local phase segregation. In contrast, solution-processed techniques such as slot-die coating provide a reservoir to ensure proper mixing of inks before deposition on a substrate.

Finally, high-throughput characterization techniques are yet to be developed to study the local properties of thin films. It is already possible to measure optical properties (absorption and photoluminescence) in a high-throughput manner. However, measuring local composition (e.g., by X-ray fluorescence), structure (e.g., by X-ray diffraction), or electrical properties (e.g., by the four-point probe) remains time-consuming.

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Author Contributions

The manuscript was written through the contributions of all authors. All authors have approved the final version of the manuscript.

Notes

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